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THE EFFECT OF ONE SALT UPON THE HYDRATING POWER OF ANOTHER SALT PRESENT IN THE SAME SOLUTION.

DISSERTATION

Submitted to the Board of University Studies of the
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By

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THE EFFECT OF ONE SALT

UPON

THE HYDRATING POWER OF ANOTHER SALT

PRESENT IN THE SAME SOLUTION.

Eight years ago Jones and Ota[1] and Jones and Knight[2] observed that certain salts in concentrated solution, give abnormally great lowering of the freezing-point of water. The problem was taken up experimentally by Jones and Chambers[3] and studied for a number of chlorides and bromides. As a result of this work Jones[4] concluded that "In concentrated solutions these chlorides and bromides must take up part of the water, forming complex compounds with it, and thus removing it from the field of action as far as freezing-point lowering is concerned. The compound, which is probably very unstable, formed by the union of a molecule of the chloride or bromide with a large number of molecules of water, acts as a unit or as one molecule in lowering the freezing-point of the remaining water. The total amount of water present, which is now acting as solvent, is diminished by the amount taken up by the chloride or bromide molecules. The lowering of the freezing-point is thus abnormally great, because a part of the water is no longer present as solvent, but is

1. Amer. Chem. Journ., 22, 5 (1899).
2. Ibid., 22, 110 (1899).
3. Ibid., 23, 89 (1900).
4. Ibid., 23, 103 (1900).

in combination with the chloride or bromide molecules."

A large amount of work on this problem has since been carried on in this laboratory and nineteen papers[1] have already been published by Jones and his coworkers in this laboratory on the combination of solvent and dissolved substance. We shall not attempt to review the work already done, but shall merely state briefly the lines of evidence developed for the hydrate conception, and then proceed to the consideration of our particular phase of the problem.

Five distinct lines of evidence bearing upon the hydrate theory have been pointed out: First, the minima in the boiling-point curves manifest themselves at greater concentrations than in the freezing-point curves. "This is just

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1. Jones and Chambers: Amer. Chem. Journ., 33, 189 (1900).
Chambers and Frazer: Ibid., 23, 512 (1900).
Jones and Getman: Ibid., 27, 433 (1902).
" " " : Ztschr. phys. chem., 46, 244 (1903); Phys. Rev., 18, 146 (1904).
Jones and Getman: Amer. Chem. Journ., 31, 303 (1904).
" " " : Ztschr. phys. chem., 49, 385 (1904).
" " " : Ber. d. chem. Ges., 37, 1511 (1904).
" " " : Amer. Chem. Journ., 32, 308 (1904).
" " " : Ibid., 32, 338 (1904).
Jones and Bassett: Amer., Chem. Journ., 33, 534 (1905).
" " " : " " " 34, 290 (1905); J. chim. Phys., 3, 455 (1905).
Jones and Bassett: Z. phys. chem., 53, 261 (1905).
" ---------- " " " 55, 385 (1906).
Jones and McMaster: Amer. Chem. Journ., 35, 136 (1906).
" ----------: " " " 35, 445 (1906).
" ----------: Monograph #60, Carnegie Inst.

what would be expected in terms of our hydrate theory, since, at the higher temperature, the hydrates would be less stable and a greater concentration would have to be reached before there would be sufficient hydration to change the direction of the curve and produce a minimum."

Second; the relation between water of crystallization and lowering of freezing-point.[1] Hydrating power is a function of water of crystallization— the larger the number of molecules of water of crystallization the greater, in general, is the hydrating power of the salt. The water of crystallization may be taken as roughly proportional to the hydrating power of the substance.

Third; the complexity of the hydrates, as well as the number of molecules of water of crystallization varies with the temperature.[2]

Fourth; certain color changes[3] which take place in solution, e.g. the change in color of a solution of cobalt chloride from a typical purplish red to a beautiful blue when treated with a small amount of some other salt with large hydrating power, such as calcium chloride or aluminium chloride. This effect of water of hydration upon the

1. Amer. Chem. Journ., 31, 344 (1904); Ztschr. phys. chem., 49, 385 (1904); Amer. Chem. Journ., 32, 308 (1904); 33, 534 (1905); J. chim. Phys., 3, 455 (1905).
2. Amer. Chem. Journ., 34, 293 (1905).
3. " " " , 34, 290 (1905).

vibration of the dissolved particles is shown by the spectrograms of various binary mixtures of salts.[1]

Fifth; the temperature coefficients of conductivity[2] of aqueous solutions of electrolytes are greater, the greater the hydrating power of the electrolyte. The temperature coefficients of conductivity of aqueous solutions of electrolytes are of the same order of magnitude for those solutions having, approximately, the same hydrating power. The temperature coefficients of conductivity for any given substance increase with the dilution of the solution, and this increase is greatest for those substances with large hydrating power, just as would be expected from the hydrate theory.

Assuming, then, the existence of hydrates to be sufficiently well established by the work referred to above, it seemed desirable to attempt to determine, if possible, the effect of one salt with hydrating power upon the hydrate formed by a second salt in the same solution. Also the effect upon the hydrates formed by a salt, when there is present in the same solution a second salt with very small hydrating power. When both salts possess the power of forming

1. Amer. Chem. Journ., [illegible] (1907); Monograph #60, Carnegie Inst.
2. Amer. Chem. Journ., 35, 445 (1906).

hydrates in single solution, the amounts of water taken up by the salts at the same concentrations may be the same, or vary within wide limits. We proposed to study binary mixtures in which both conditions are illustrated.

Since we desired to calculate the approximate composition of the hydrates formed in the mixtures, as nearly as possible, it was necessary to obtain data for the freezing-points, conductivities, and number of grams of solvent in a litre of solution of the various salts employed. In order that we might have the data for the exact normalities of the solutions which we mixed, it seemed advisable to make the necessary measurements in the single solutions, rather than to attempt to interpolate from data previously obtained.

CONDUCTIVITY CALCULATIONS.

It is well known that when two or more electrolytes are present in the same solution, the conductivity of this solution is not equal to the sum of the conductivities which these electrolytes have in separate solutions of the same normality as that which these salts may be assumed to have in the mixture; but that the conductivity of the mixture is generally less than this sum. If the solutions are isohydric[1], that is, the component solutions possess a common

1. Arrhenius: Wied. Ann., 30, 51 (1887); Ztschr. phys. chem., 2, 284 (1888).

ion in equal concentration, then the simplest conditions prevail between the conductivities of the single solution and that of the mixture. This latter condition exists when

$$\frac{\alpha_1}{v_1} = \frac{\alpha_2}{v_2},$$

in which α_1 is the dissociation of one of the electrolytes at the dilution v_1, and α_2 is the dissociation of the other electrolyte at the dilution v_2. Such solutions can be mixed in any proportion without altering their dissociation, and hence the conductivity of the mixture is the mean of the conductivities of the component solutions, and can, therefore, be calculated according to the following formula:

$$k = \frac{k_1 P + k_2 P'}{P + P'},$$

in which k_1 and k_2 are the conductivities, and P and P' the proportions of the component solutions.

Unfortunately, we have to deal with no such simple relations as this in the mixtures with which we worked. If both electrolytes have a common ion and each is a weak electrolyte, then they would obey the law of mass action. Wekeman[1] and Larmwater[2] have approached this case from the standpoint of isohydrism.

Wolf[3] has investigated the conductivity of mixtures

1. Ztschr. phys. chem., 15, 159 (1894).
2. " " " , 45, 557 (1903).

of dilute solutions of strong electrolytes, with solutions of weak electrolytes. Schrader[4] has calculated the degree of dissociation of each electrolyte, from considerations of the transport numbers of the ions, the quantities of the anions and the cations migrating to their respective poles, the quantities of each separated at the electrodes, etc. Hoffmeister[5] and Hopfgartner[6] have dealt with the concentrations of the cations in a mixture of two electrolytes. Noyes and Kerr[7] indicate a method of ascertaining the dissociation of the salts in a mixed solution, which they apply to the solutions with which they had to deal. Barnwater's[8] equations take into consideration the viscosity of the solution, the friction between the ions and the solvent, and between the ions themselves, the normality, dissociation, current employed, etc., and give a satisfactory agreement between calculated and experimental results. MacGregor[9] and his students have also carried out considerable

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4. Ztschr. Electrochem. 3, 498 (1897).
5. " phys. chem., 27, 345 (1898).
6. " " " , 25, 115 (1898).
7. Journ. Chem. Soc., 24, 1148 (1902).
8. Ztschr. phys. chem., 28, 426 (1899).
9. Trans. N. S. Inst. of Sc., 10, (1898 - 99); 9, 101 (1895 - 96); Phil. Mag., 41, 270 (1896); Trans. Roy. Soc. Can., 3, sect. 3, 65 (1896 - 97).

work upon the conductivities of mixed electrolytes, solving the equations deduced by a graphical method.

In our work, however, the viscosity of the mixtures differs considerably, in many cases, from that of the single solutions assumed to have the same normality. This would involve changes in friction in the movement of the ions. Also, the amount of water combined as hydrate, i. e., the dimensions of the atmosphere about the ion, continually changed from one normality to another. This involved a varying degree of freedom of movement of the ions. Again, the variation in the number of particles present, ions and molecules, must involve continual variation in the amount of friction between the ions. As a comparatively short, and at the same time sufficiently accurrate method, we have adopted the following in apportioning the diminution in conductivity to the constituent salts:— Since we have dealt with mixtures in which the two electrolytes have a common ion in every case, we have based the method on the number of this common ion yielded by the constituent salts in separate solutions at the same normality. By the same normality we mean that if equal volumes of two solutions are mixed, and any diminution in volume which may take place

upon mixing is compensated for by the addition of pure solvent, then the normality of each solution in the mixture may be assumed to be exactly half of that of the constituent solutions. If suppression of the ionization is dependent upon the common ion, then it will be inversely as the number of this common ion furnished by each of the salts in a mixture. This number was obtained thus:— The figure representing the normality of the individual solutions, multiplied by the value of α for the solution at the normality in question, would give the gramme atomic weight of the common ion. Suppose the case to be one where a solution of potassium chloride has been combined with an equal volume of a solution of calcium chloride. It being assumed that calcium chloride dissociates into

$$\overset{++}{Ca}, \text{and } \overset{-}{Cl}, \overset{-}{Cl},$$

this figure representing the gramme atomic weight of the common ion would have to be doubled for a ternary electrolyte, such as calcium chloride. Since two chlorine ions are required to re-form a molecule of calcium chloride, the figure expressing the number of chlorine ions driven back in the case of calcium chloride must be divided by two, in order to get the relative number of molecules of calcium chloride re-formed.

Let us take the values of Λ_∞ as expressing the molecular conductivity of the completely dissociated molecules of the various salts. If the figures for the relative numbers of molecules of the two salts re-formed, be multiplied by the proper value of Λ_∞, we shall then have the relative losses in conductivity. From this the absolute losses are readily obtained. An example may suffice to make this clear:- Take the case of the mixture of equal volumes of a solution of 1.8 N. calcium chloride and of 1.7 N. potassium chloride. The resulting solution, any diminution of volume having been compensated for, will consist of 0.9 N. calcium chloride and 0.85 N. potassium chloride. The dissociation of a 0.9 N. solution of the specimen of calcium chloride employed was found by conductivity measurements to be 58.2%; of 0.85 N. potassium chloride, 83.2%. Doubling the value of α in the case of calcium chloride and multiplying by the normality, we get 0.9576. Similarly, for potassium chloride, 0.7068. These represent the relative numbers of chlorine ions which would be furnished by each salt in the mixture, if no suppression of the ionization took place upon mixing. That is, if driving back occurs, according to the law of mass action, 70% chlorine ions

should be driven back to re-form calcium chloride; to 15% for potassium chloride. But since it requires two ions of chlorine to re-form each molecule of calcium chloride, only 154 molecules of calcium chloride will be re-formed to every 588 molecules of potassium chloride. Multiplying these values by Λ_∞ for calcium chloride and potassium chloride respectively, we get 5422, approximately, for calcium chloride; and 7095 for potassium chloride. These values represent the relative losses in conductivity upon mixing. From this the decrease in conductivity can be apportioned between the two salts.

All conductivity measurements are given as specific conductivities in the mixtures. The units employed are reciprocal centimetre ohms. For purposes of comparison with the previous work upon the "Hydrate theory" our units may be transformed by dividing Λ_v by 1.0[illegible].[1] This would give μ_v for the same liquid.

The compositions of the hydrates in the <u>single</u> solutions was calculated by the method previously employed by Jones[2] and his coworkers.

EXPERIMENTAL WORK.

FREEZING POINT. The more concentrated solutions were frozen by means of a mixture of solid carbon dioxide and alcohol, the freezing temperature being determined by means of alcohol thermometers. These temperatures could not be measured more closely than 0°.5. For the more dilute solut-

ions freezing mixtures of ice and sodium chloride, or ice and crystallized calcium chloride were employed. The temperatures were read by means of Beckmann thermometers, covering a range of 6°, 12° and 25° respectively. When the more concentrated solutions were frozen they were removed from the bath of solid carbon dioxide and alcohol as [illegible] began to separate, in order that they might not be surrounded by the very cold freezing mixture while temperature equilibrium was being established. The necessary correction for the separation of ice and consequent increase in concentration was introduced in every instance. The separation of some of the dissolved substance was readily ascertained by the grit or sand like character of the solid that separated, which was easily detected. Since it was found that in the volume of liquid emplyed in the freezing-point tube, about twenty-five cubic centimeters, a freezing-point determination made with a large undercooling, and consequent copious separation of ice, gave somewhat different results from one where the undercooling was less, care was taken

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1. "The Conductivity of Liquids," O. F. Tower, pages 2 et seq.
2. Amer. Chem. Journ., 34, 298 (1905); Amer. Chem. Journ., 33, 543 (1905).

both in the freezing-point determinations of the pure solvent and of the solutions, to keep the undercooling nearly the same:— about a degree, throughout. This necessitated inoculating the solution with an exceedingly minute particle of the solid phase of the solvent, in nearly every case.

CONDUCTIVITY.

Conductivities were measured by the method of Kohlrausch, employing a Wheatstone bridge, telephone receiver and induction coil. The bridge wire was of "manganin" and was calibrated before beginning the work, by the method of Strouhal and Barus.[1]

The resistance coils, manufactured by Leeds and Co., were tested and found in no case to involve a greater error than 0.04 per cent.

The dilute solutions were measured in conductivity cells of the form employed by Jones and McMaster,[2] the tubes carrying the platinum electrodes being sealed into both the upper and lower walls of the stopper. For the more concentrated solutions cells of the type used by Jones and Getman[3]

1. Wied. Ann., 10, 326 (1880).
2. Amer. Chem. Journ.
3. Ztschr. phys. Chem., 46, 254 (1903).

were employed. The electrodes were treated in the usual manner (coated with platinum black, etc.), in order to obtain a sharper tone minimum or point of silence in the readings.

The cells for the more dilute solutions were standardized by determining the cell constant by means of N/50 potassium chloride. The value k = .0015148 was taken as the conductivity of N/50 potassium chloride. For the more concentrated solutions the cell constants were determined with a N/2 solution of potassium chloride, for which k = .03865 at 0°.[1] The potassium chloride employed in determining cell constants was recrystallized five times, the last two times from conductivity water, and was free from all impurities. The cell constants were frequently redetermined, but very little change in them was noted from time to time. The cells were filled with distilled water when not in use, and were always carefully cleansed, dried, and rinsed with the new solution when a change in solutions was made. All conductivities were measured at 0°. The temperature of the zero bath was always within a tenth of a degree of 0° as determined by an accurately standardized thermom-

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[1] These values are calculated from the results of Jones and West. See Amer. Chem. Journ., 34, 381 (1905).

eter. All conductivity measurements are the average of four measurements with differing resistances in circuit.

The water used in this work was purified thus: Ordinary distilled water was redistilled from potassium dichromate and sulphuric acid. This was then again distilled from a second flask containing acidified potassium dichromate, and the steam led through a boiling solution of barium hydroxide and condensed in a block tin condenser. The water purified as above had a conductivity of 1.2 to 2.5 x 10^{-6} at 0°.

It is well known that the conductivity method is not an accurate measure of dissociation in concentrated solutions. Especially is this the case at the concentrations with which we dealt, since in the mixtures we have employed, the values of Λ_∞ were determined for each salt by diluting the single solution to a maximum value of Λ_ν, as the value which Λ_∞ would exhibit in the mixture. This is, obviously, a source of additional error, for the conductivity of the ions resulting from a completely dissociated molecule in a very dilute solution must be different from the conductivity of these ions in a more concentrated solution. In the more dilute solution a larger atmosphere of the solvent is attached to the ions, and this must be dragged along by

them. There is a much smaller number of particles of salt (ions or molecules), present in the dilute solution than in the more concentrated. Consequently the friction between the ions in their movements must be different. The viscosity of the solutions in which Λ_∞ can be determined is very much less than the viscosity of the solutions at the concentrations employed. These are all important factors which affect the conductivity of any dissolved substance. The method is, however, an approximate one for measuring such dissociations and is the best we can do at present. All that can be said is, that it probably gives values of the right order of magnitude.

CALCIUM CHLORIDE.

A strong mother solution of Calcium chloride was made up and standardized by precipitating the calcium in a known volume, and from this calculating the amount of calcium chloride present. All solutions were made up by diluting the calculated amount of this mother solution to the required volume.

Table I. FREEZING-POINT MEASUREMENTS.

m.	Δ.	Δ/m.
0.3	1°517	5°056
0.5	2.672	5.344
0.6	3.270	5.450
0.7	4.065	5.807
0.9	5.422	6.024
1.0	6.410	6.410
1.1	7.080	6.436
1.35	9.362	6.934
1.4	10.05	7.18
1.55	11.58	7.47
1.755	14.33	8.16
1.88	14.69	8.16
2.3	21.07	9.58
2.7	30.25	11.20
3.1	39.5	12.74
3.5106	49.5 ?	14.10 ?

In this table, as elsewhere where they occur, m is the concentration in terms of gram molecules per liter: Δ the observed freezing-point lowering, corrected for the separation of ice, and Δ/m the molecular lowering of the freezing-point.

Table II. CONDUCTIVITY MEASUREMENTS.

Λ_{∞}, 0° = 147.52.[1]

m.	v.	k.	Λ_v.	α.
0.3	3.333	.026044	98.5	.674
0.5	2.000	.043401	87.0	.594
0.6	1.6666	.050268	83.8	.568
0.7	1.4285	.057555	82.2	.557
0.9	1.1111	.070601	78.4	.532
1.0	1.000	.07554	75.5	.512
1.1	0.909	.081573	74.1	.502
1.35	0.7407	.092660	68.6	.466
1.4	0.7143	.09396	67.1	.455
1.55	0.6453	.099184	64.0	.434
1.755	0.5698	.10723	61.1	.414
1.8	0.5555	.107367	59.8	.405
2.2	0.4545	.115676	52.7	.357
2.7	0.3704	..7757	45.6	.309
3.1	0.3226	.11410	36.8	.250
3.5106	0.2849	.10710	30.5	.207

In this table, as elsewhere throughout this paper, m is the concentration, in terms of gram-molecules per litre; v is the number of liters that contain a gram-molecule of the dissolved substance; k is the specific conductivity,

1. Calculated from the value given by Jones and Bassett; Amer. Chem. Journ., 33, 547 (1905).

and is equal to

$$\frac{\mu_v \times .001005}{v};$$

Λ_v is the molecular conductivity at 0°, and is equal to 1000 x v x k; α is the per cent of dissociation, and is equal to $\Lambda_v / \Lambda_\infty$.

Table III. WEIGHT-MOLAL CORRECTIONS, or Number of Grams of Solvent in a 1000 cubic centimeters of Solution.

M.	W Sol.	W Salt	W H_2O	Correction Per Cent.
0.3	51.270	1.665	49.605	0.8
0.5	52.2608	2.775	49.4858	1.0
0.6	52.7437	3.33	49.4137	1.2
0.7	53.1162	3.885	49.2312	1.5
0.9	53.9816	4.995	48.9866	2.0
1.0	54.3[illegible]6	5.55	48.776	2.4
1.1	54.772	6.105	48.667	2.7
1.35	55.9455	7.4925	48.451	3.1
1.4	56.115	7.770	48.345	3.3
1.55	56.6562	8.6025	48.0537	3.9
1.755	57.7040	9.7402	47.9638	4.1
1.8	28.900	4.995	23.905	4.1
2.2	29.650	6.105	23.545	5.8
2.7	30.682	7.492	23.190	7.3
3.1	31.461	8.402	23.059	8.6
3.5106	32.187	9.720	22.467	10.1

In these tables of weight-normal corrections, m has the usual significance; $W_{Sol.}$ is the weight of twenty-five or of fifty cubic centimeters of the solution; W_{Salt} is the weight of salt contained in this volume of the solution; W_{H_2O} is the weight of water in this volume of solution, equal to $W_{Sol.} - W_{Salt}$; Correction Per Cent is the percentage correction to be applied in order to refer measurements to a thousand grams of solvent. These are not specific gravity measurements made in pycnometers, and we therefore give the correction per cent only to the first decimal.

In the following table, as in all other tables of the hydrates formed in the single solutions, m has the usual significance; α is the per cent of dissociation; L is the theoretical molecular lowering of the freezing-point referred to a thousand grams of the solvent; Δ/m the molecular lowering found experimentally; L' the molecular lowering, h the number of gram-molecules of water in combination, both being referred to a thousand grams of solvent;

$$h = \frac{1000 - \frac{L}{L'} \times 1000}{18};$$

H is the number of molecules of water in combination with one molecule of the salt, at the concentration in question, if a liter of the solution at that concentration, contained a thousand grams of water: it equals $\frac{h}{m}$.

Table IV. HYDRATES.

m.	α.	L.	Δ/m.	L'.	M.	H.
0.3	.674	4.22	5.06	5.02	8.8	29.4
0.5	.594	4.09	5.34	5.29	12.6	25.2
0.6	.568	3.97	5.45	5.39	14.6	2 .3
0.7	.557	3.93	5.81	5.72	17.4	24.8
0.9	.532	3.84	6.02	5.90	19.4	21.6
1.0	.512	3.76	6.31	6.16	21.6	"
1.1	.502	3.73	6.44	6.26	22.4	20.4
1.35	.466	3.59	6.93	6.72	25.9	19.2
1.4	.455	3.55	7.18	6.94	27.2	19.4
1.55	.434	3.47	7.47	7.18	28.7	16.5
1.755	.414	3.40	8.16	7.83	31.4	17.9
1.8	.405	3.37	"	7.80	31.6	17.5
2.2	.357	3.19	9.58	9.03	35.9	16.3
2.7	.296	2.96	11.20	10.39	39.7	14.7
3.1	.259	2.79	12.74	11.65	43.6	14.1
3.5106	.207	2.63	14.10	12.68	46.5	13.2

Since we wished to investigate the effect of the presence of a salt with little hydrating power upon a salt with considerable hydrating power, potassium chloride was added to calcium chloride. The data for the various solutions of potassium chloride alone are therefore given next.

POTASSIUM CHLORIDE.

Table V. FREEZING-POINT MEASUREMENTS.

m.	Δ.	Δ/m.
0.45	1°52	3°35
0.65	2.24	3.45
0.85	2.91	3.43
.90	3.08	3.42
1.05	3.58	3.41
1.2972	4.46	3.45
1.3	4.49	3.46
1.7	5.93	3.49
2.1	7.43	3.54
2.5945	9.29	3.58

Table VI. CONDUCTIVITY MEASUREMENTS.
Λ_∞, 0° = 80.88.[1]

m.	v.	k.	Λ.	α.
0.45	2.233	.050882	67.4	.839
0.65	1.538	.043608	67.1	.835
0.85	1.1765	.050804	66.6	.832
0.90	1.1111	.053717	65.2	.812
1.05	0.9523	.061969	65.7	.818
1.2972	0.7709	.082948	64.7	.805
1.3	0.7692	.084118	"	"
1.7	0.5882	.109202	64.2	.800
2.1	0.4762	.133785	63.7	.793
2.5945	0.3851	.162207	62.8	.782

Table VII. WEIGHT-NORMAL CORRECTIONS.

m.	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction PER CENT.
0.45	8.0042	0.26353	7.74067	1.4
0.65	8.0735	0.38066	7.69281	2.0
0.85	8.1443	0.49654	7.64766	2.6
0.90	25.9936	1.6785	24.3151	2.7
1.05	8.2169	0.61492	7.60198	3.2
1.3	26.5127	2.4345	24.0682	3.7
1.7	26.928	3.1705	23.7575	5.0
2.1	27.4457	3.9165	23.5292	5.9
2.5945	28.0254	4.8385	23.1869	7.3

Table VIII. HYDRATES.

m.	α.	L.	Δ/m.	L'.	M.	H.
0.45	.829	3.42	3.75	3.30		
0.65	.835	3.41	3.45	3.38		
0.85	.832	"	3.43	3.34		
0.90	.812	3.37	3.42	3.32		
1.05	.818	3.38	3.41	3.40		
1.3[1]	.805	3.36	3.45	3.33		
1.3	"	"	3.36	"		
1.7	.800	3.35	3.49	3.31		
2.1	.793	3.34	3.54	3.33		
2.5945	.782	3.32	3.58	3.32		

Evidently no hydrating power.

1. Calculated from the value given by Jones and West; Amer. Chem. Journ., 3 , 381 (1905).

MIXTURES OF CALCIUM CHLORIDE AND POTASSIUM CHLORIDE.

Table IX. FREEZING-POINT MEASUREMENTS.

m.	P.	Δ.
1.0 Ca_2Cl 0.9 K Cl	1 "	4°.418
1.4 Ca Cl_2 1.3 K Cl	1 "	6.625
1.8 Ca Cl_2 1.7 K Cl	1 "	9.17
2.2 Ca Cl_2 2.1 K Cl	1 "	12.01
2.7 Ca Cl_2 2.5945 K Cl	1 "	15.00
3.1 Ca Cl_2 2.5945 K Cl	1 "	16.50
3.5106 Ca Cl_2 2.5945 K Cl	1 "	18.0

Column headed P indicates parts by volume of each solution which were mixed; m is the normality of the solutions before mixing; In order that each solution should have exactly one-half the normality after mixing which it had before, the volume of the mixture was brought to exactly twice the volume of either constituent solution.

TABLE X. CONDUCTIVITY MEASUREMENTS.

n.	P.	n_c.	v_c.	K_w.	k.	D.	K_c.	Λ_v	α.
1.0 $CaCl_2$	1	0.5	2.000	.069077	.048301	.004156	.04283	84.6	.572
0.9 KCl	"	0.45	2.222		.030352		.027697	61.5	.736
1.4 $CaCl_2$	1	0.7	1.4285	.093713	.057655	.00745	.054653	72.1	.593
1.3 KCl	"	0.65	1.538		.049608		.039060	60.0	.743
1.3 $CaCl_2$	1	0.9	1.1111	.114096	.070601	.012809	.065221	72.5	.491
1.7 KCl	"	0.85	1.1765		.056804		.048875	52.5	.716
		1.05							
2.2 $CaCl_2$	1	1.1	0.909	.13081	.081573	.01973	.078653	66.7	.458
2.1 KCL	"	1.05	0.9523		.063069		.057459	54.7	.691
2.7 $CaCl_2$	1	1.35	0.7407	.14805	.092860	.02876	.08041	52.6	.404
2.5945 KCl	"	1.2972	0.7703		.092949		.06765	52.2	.642
2.1 $CaCl_2$	1	1.05	0.9451	.15081	.090184	.03282	.087734	55.4	.875
2.5945 KCl	"	1.2972	0.7703		.088049		.065018	50.1	.694
2.5108 $CaCl_2$	1	1.255	0.5808	.15283/.10728		.03279	.09183	52.9	.855
2.5945 KCl	"	1.2972	0.7703		.088049		.06058	46.7	.581

N is the normality of the solutions mixed. P is the parts by volume of each solution which were mixed. When equal volumes are mixed the resulting normality of each solution is exactly one-half of that of the solutions before mixing. This is given under n_c. V_c is number of liters of solution which will contain a gram molecular weight of the salt, based on n_c. K_u is the specific conductivity of the mixture. This would be the sum of the conductivities of the component solutions if no suppression of the ionization occurred. K gives the conductivities of the single solutions of each salt at the normality acquired upon mixing. In each case the sum of these two, minus the conductivity of the mixture, k_u, gives the decrease in conductivity due to the driving back of the dissociation of the salts in question. This is given under D. This loss in conductivity is then apportioned to each electrolyte by the method already described, and the resulting conductivities are given under K_c. From this, Λ_v and α are obtained.

Table XI. WEIGHT-TOTAL CONCENTRATIONS.

m.	P.	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction Per Cent
1.0 CaCl 0.9 KCl	1 "	26.7148	2.22657	24.51843	1.9
1.4 CaCl 1.3 KCl	1 "	27.3662	3.1542	24.3120	3.2
1.8 CaCl 1.7 KCl	1 "	28.0354	4.0627	23.9727	4.2
2.2 CaCl 2.1 KCl	1 "	28.6177	5.0102	23.6075	5.6
2.7 CaCl 2.5945 KCl	1 "	29.422	6.1655	23.2565	6.9
3.1 CaCl 2.5945 KCl	1 "	29.8247	6.7205	23.1042	7.6
3.5106 CaCl 2.5945 KCl	1 "	30.2118	7.2793	22.9325	8.3

Proceeding upon the tentative hypothesis that the calcium chloride forms the same hydrates in the presence of a salt with no hydrating power, that it forms in separate solution, Tables XII and XIII are prepared.

Table XII. CALCIUM CHLORIDE IN THE MIXTURE.

m.	P.	m_c.	α.	L.	I.
1.0 $CaCl_2$ 0.9 KCl	1 "	0.5	.576	3.192	2.034
1.4 $CaCl_2$ 1.3 KCl	1 "	0.7	.549	3.829	2.769
1.8 $CaCl_2$ 1.7 KCl	1 "	0.9	.491	3.687	3.464
2.2 $CaCl_2$ 2.1 KCl	1 "	1.1	.452	3.541	4.126
2.7 $CaCl_2$ 2.5945 KCl	1 "	1.35	.404	3.362	4.88
3.1 $CaCl_2$ 2.5945 KCl	1 "	1.55	.375	3.256	5.462
3.5106 $CaCl_2$ 2.5945 KCl	1 "	1.7553	.355	3.179	6.084

α is the dissociation of the calcium chloride in the mixture. L is the freezing-point lowering calculated from the formula $(1.86 \times 2\alpha) + 1.86$. I is the freezing-point lowering, corrected to one thousand grams of solvent, which the salt would give if ther were no hydration.

m.	P.	m_c.	α.	Δ.	W_{H_2O}	Correction Per Cent	I.
1.0 CaCl 0.9 KCl	$\frac{1}{n}$	0.45	.766	1.478	755.7	2[illegible].6	1.961
1.4 CaCl 1.3 KCl	$\frac{1}{n}$	0.65	.748	2.113	655.9	34.4	3.222
1.8 CaCl 1.7 KCl	$\frac{1}{n}$	0.85	.716	2.712	608.2	39.2	4.454
2.2 CaCl 2.1 KCl	$\frac{1}{n}$	1.05	.681	3.283	538.5	46.2	6.097
2.7 CaCl 2.5945 KCl	$\frac{1}{n}$	1.2972	.649	3.068	464.7	53.5	8.564
3.1 CaCl 2.5945 KCl	$\frac{1}{n}$	1.2972	.624	3.021	408.0	59.2	9.605
3.5106 CaCl 2.5945 KCl	$\frac{1}{n}$	1.2972	.581	3.941	340.5	66.0	11.20

α is the dissociation of the potassium chloride in the mixture. Δ is the freezing-point lowering deduced from $[(1.86 \times \alpha) + 1.86]\, m_c$. W_{H_2O} is the weight of water acting as solvent toward the potassium chloride, deduced from:— $L : L' :: x : 1000$, which gives the amount of water taken up by the calcium chloride in the formation of hydrates when it alone is present in solution, and the weight-normal correction for the mixture. I is the ideal lowering the potassium chloride would give if the calcium chloride formed the same hydrates in the mixture that it forms when alone in solution.

Table XIV. Comparison of lowerings due to hydration in separate solution of CALCIUM CHLORIDE and in the mixture.

m.	P.	m_c.	Δ_c.	I_c	$Diff_c$.	Δ.	I	Diff.
1.0 CaCl 0.9 KCl	$\frac{1}{n}$	0.5	4.413	3.995	0°418	2.672	2.066	0°606
1.4 CaCl 1.3 KCl	$\frac{1}{n}$	0.7	6.625	5.991	0.634	4.004	2.75	1.25
1.8 CaCl 1.7 KCl	$\frac{1}{n}$	0.9	9.170	7.918	1.252	5.314	3.455	1.859
2.2 CaCl 2.1 KCl	$\frac{1}{n}$	1.1	12.01	10.223	1.782	6.896	4.100	2.796
2.7 CaCl 2.5945 KCl	$\frac{1}{n}$	1.35	15.0	13.442	1.558	9.072	4.851	4.221
3.1 CaCl 2.5945 KCl	$\frac{1}{n}$	1.55	16.5	15.067	1.433	11.13	5.385	5.745
3.5106 CaCl 2.5945 KCl	$\frac{1}{n}$	1.7553	18.0	17.288	0.712	14.10	5.97	8.13

Δ_c is the lowering found experimentally for the mixture. I_c is the sum of I in Tables XII and XIII. $Diff_c$ = $\Delta_c - I_c$ = lowering due to hydration. Δ is lowering found experimentally for calcium chloride, corrected to one thousand grams of solvent. I is the lowering the calcium chloride should have given in 1000 grams of solvent, if there were no hydration. Evidently $Diff_c$ and Diff should be identical if there were no change in hydration. Such is not the case. Consequently, the basis assumed for the calculation of I for Potassium chloride in the mixture is incorrect, since it

depends upon a knowledge of the amount of water eliminated from the sphere of action as solvent, by the hydration of the calcium chloride. It, therefore, becomes necessary to derive a formula for the calculation of the hydration of the calcium chloride, in the mixture.

Formula for Calculating lowering due to Hydration, in a Binary Mixture of Electrolytes, where One Salt has no Hydrating Power.

Let $x°$ equal lowering due to hydration of the salt with hydrating power, in the mixture.

I = ideal lowering which the salt with hydrating power should give in the mixture in question, at the corrected dissociation, if there were no hydration.

v = number of litres which contain a gram molecule of the salt with hydrating power, at the normality it has in the mixture.

Then $(x + I)v = \Delta/m$.

S = Correction to 1000 grams of solvent, necessary in the mixture.

$(x + I)v - (x + I)vS = L'$.

x' = amount of water acting as solvent toward the salt with no hydrating power.

$L : L' :: x' : 1000$.

$L = (1.86 \times 2\alpha) + 1.86$, in a ternary electrolyte,

where α represents the corrected dissociation of the salt with hydrating power, in the mixture.

$$\frac{(1.86 \times 2\alpha) + 1.86}{(x + I)v - (x + I)vS} \cdot 1000 = x'.$$

But taking into account the weight-normal correction also, in the mixture in question, the above becomes,

$$\left[\frac{(1.86 \times 2\alpha) + 1.86}{(x + I)v - (x + I)vS} \cdot 1000\right] - 108 = \text{amount of water actually acting as solvent toward salt with no hydrating power.}$$

Putting this into the form of a percentage correction,

$$\frac{(1.86 \times 2\alpha) + 1.86}{(x + I)v - (x + I)vS} - \frac{S}{100} = \text{the per cent by which}$$

I for the salt wth little, or no hydrating power must be divided.

Let α' = the corrected dissociation of the salt with no hydrating power, in the mixture.

$[(1.86 \times \alpha) + 1.86]m$ = lowering it would give in 1000 grams of solvent, if it is a binary electrolyte. m is the normality of the salt with no hydrating power.

$$\text{then, } \frac{1.86m(\alpha' + 1)}{\frac{1.86(2\alpha + 1)}{(x + I)(v - vS)} - \frac{S}{100}} + x + I = \text{lowering found}$$

experimentally for the mixture. From this expression the value of x may be derived.

By means of this formula the value of x has been cal-

culated for the various concentrations employed in the mixture of calcium chloride and potassium chloride, and the results are given in Table IV. The significance of the abbreviations has already been given in connection with the preceding tables.

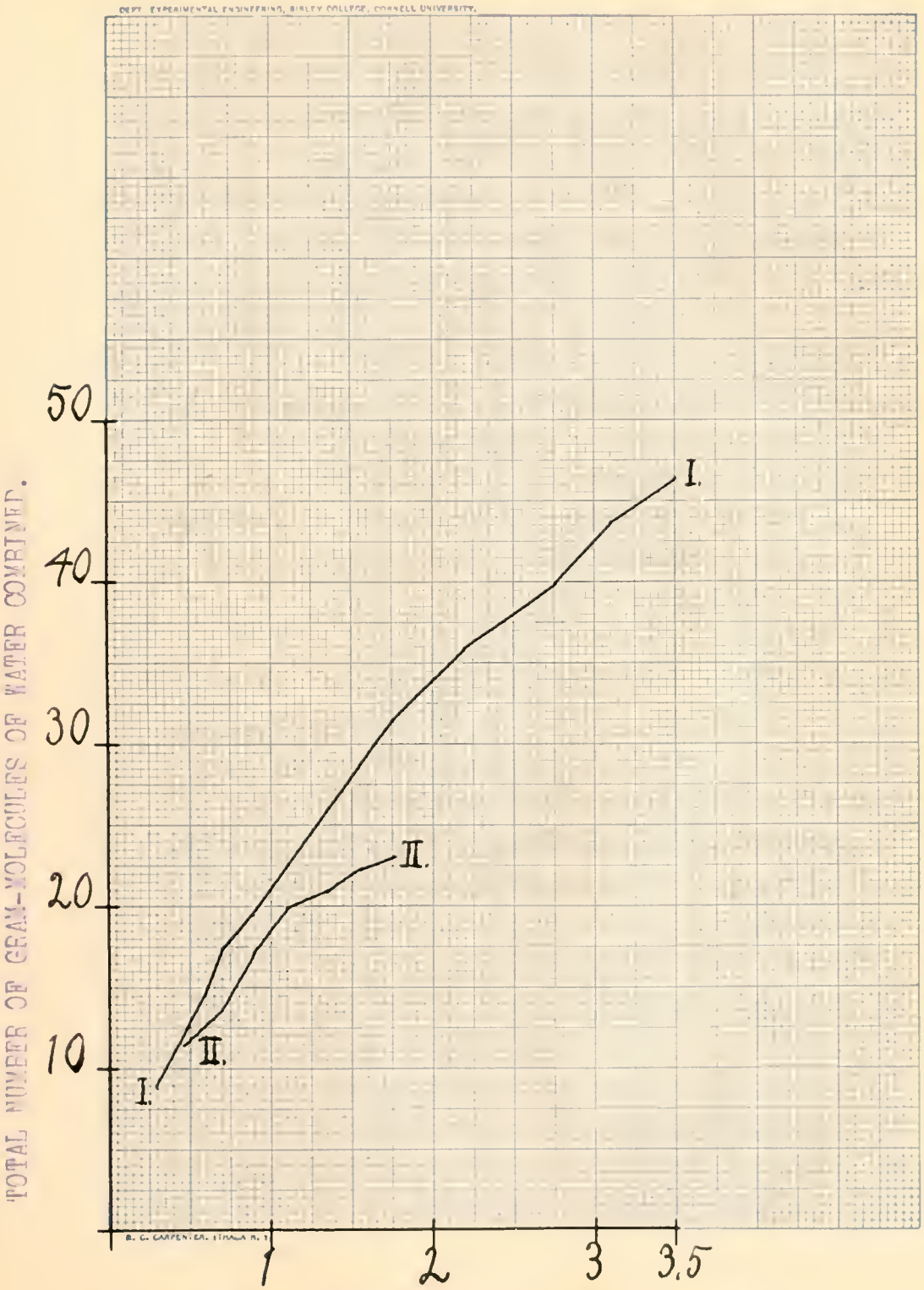
TABLE XV. HYDRATION OF $CaCl_2$ IN MIXTURE.

m.	P.	M_c.	α.	L.	I.	x.	Δ/m.	L!	M.	H.
1.0 $CaCl_2$ 0.9 KCl	1 "	0.5	.572	3.[illegible]92	2.034	0.456	4.981	4.386	10.2	[illegible]
1.4 $CaCl_2$ 1.3 KCl	1 "	0.7	.529	3.829	2.769	0.909	5.254	5.036	13.7	[illegible]
1.8 $CaCl_2$ 1.7 KCl	1 "	0.9	.491	3.687	3.464	1.537	5.556	5.333	17.1	[illegible]
2.2 $CaCl_2$ 2.1 KCl	1 "	1.1	.452	3.541	4.126	2.241	5.834	5.507	19.3	[illegible]
2.7 $CaCl_2$ 2.5945 KCl	1 "	1.35	.404	3.362	4.88	2.94	5.793	5.337	20.9	15.5
3.1 $CaCl_2$ 2.5945 KCl	1 "	1.55	.375	3.256	5.462	3.601	5.847	5.408	22.1	14.3
3.5108 $CaCl_2$ 2.5945 KCl	1.7553 "		.355	3.179	6.084	4.32	5.923	5.436	23.1	13.1

In order to compare the hydrates formed by calcium chloride in separate solution with those which it forms in the mixture with potassium chloride the values of M are plotted against the concentrations as abscissae, in Figure I.

It is seen that while the value of M increases with increase in concentration, in general, in the mixture as in separate solution, M is less in the mixture than in separate solution of calcium chloride. This is just what we should expect, since there is less water present as solvent in the mixture of calcium chloride and potassium chloride at any given concentration of the calcium chloride, than there is at the same concentration of the single solution of calcium chloride. Now it is evident from previous work that while the total number of gram-molecules of water combined increases in general, with ~~an~~ increase in concentration, the molecular hydration decreases with increase in concentration. That is, the amount of water with which a molecule of the calcium chloride or the resulting ions combine, depends upon the number of molecules of water present to one molecule of the calcium chloride. If now, instead of increasing the number of grams of salt with hydrating power, present in a given solution, thus diminish-

I. CALCIUM CHLORIDE ALONE.
II. CALCIUM CHLORIDE MIXED WITH POTASSIUM CHLORIDE.



GRAM-MOLECULES OF SALT PER LITRE OF SOLUTION.
FIGURE I.

ing the amount of water, we add to the calcium chloride a substance like potassium chloride and then make up to the former volume, it is evident that, there being less water present, the amount of water with which each molecule or ion of calcium chloride will combine will be diminished; that is, the value of M will be diminished.

In order to compare the difference between the amount of water present acting as solvent toward the calcium chloride, in the single solution and in the mixture, with the difference in the values of M in the two cases, we give in the following table, under D_{H_2O} the difference between the number of grams of water present as solvent in the separate solution of calcium chloride and in the mixture at the respective concentrations; under D_M the difference in the values of M for the separate solution of the calcium chloride and in the mixture at the same concentrations.

Table XVI.

m.	D_{H_2O}.	D_{K}.
0.5	9	2.4
0.7	17	4.8
0.9	22	2.84
1.1	29	2.61
1.35	38	4.99
1.55	" "	6.62
1.7553	42	8.36

These results are plotted in curves in Figure II.

For the first four concentrations the values of M decrease by the same amount, since the amount of potassium chloride added is increased as the calcium chloride is increased. Consequently, the curve for the difference in the values of M is approximately parallel to the axis of abscissas (concentration). Referring to Table XV it will be seen that the difference between successive values of M diminishes with increase in concentration, until finally in the mixture containing 2.7% calcium chloride and 2.5945 M potassium chloride, M has the value 20.9. The effect of the potassium chloride on the amount of water with which the calcium chloride can combine, is such that, although the

DIFFERENCE BETWEEN AMOUNT OF WATER PRESENT IN THE SINGLE SOLUTION OF CALCIUM CHLORIDE AND IN THE MIXTURE OF CALCIUM CHLORIDE AND POTASSIUM CHLORIDE

I. DIFFERENCE BETWEEN VALUES OF M FOR CALCIUM CHLORIDE IN SINGLE SOLUTION OF CALCIUM CHLORIDE AND IN MIXTURE OF CALCIUM CHLORIDE AND POTASSIUM CHLORIDE.

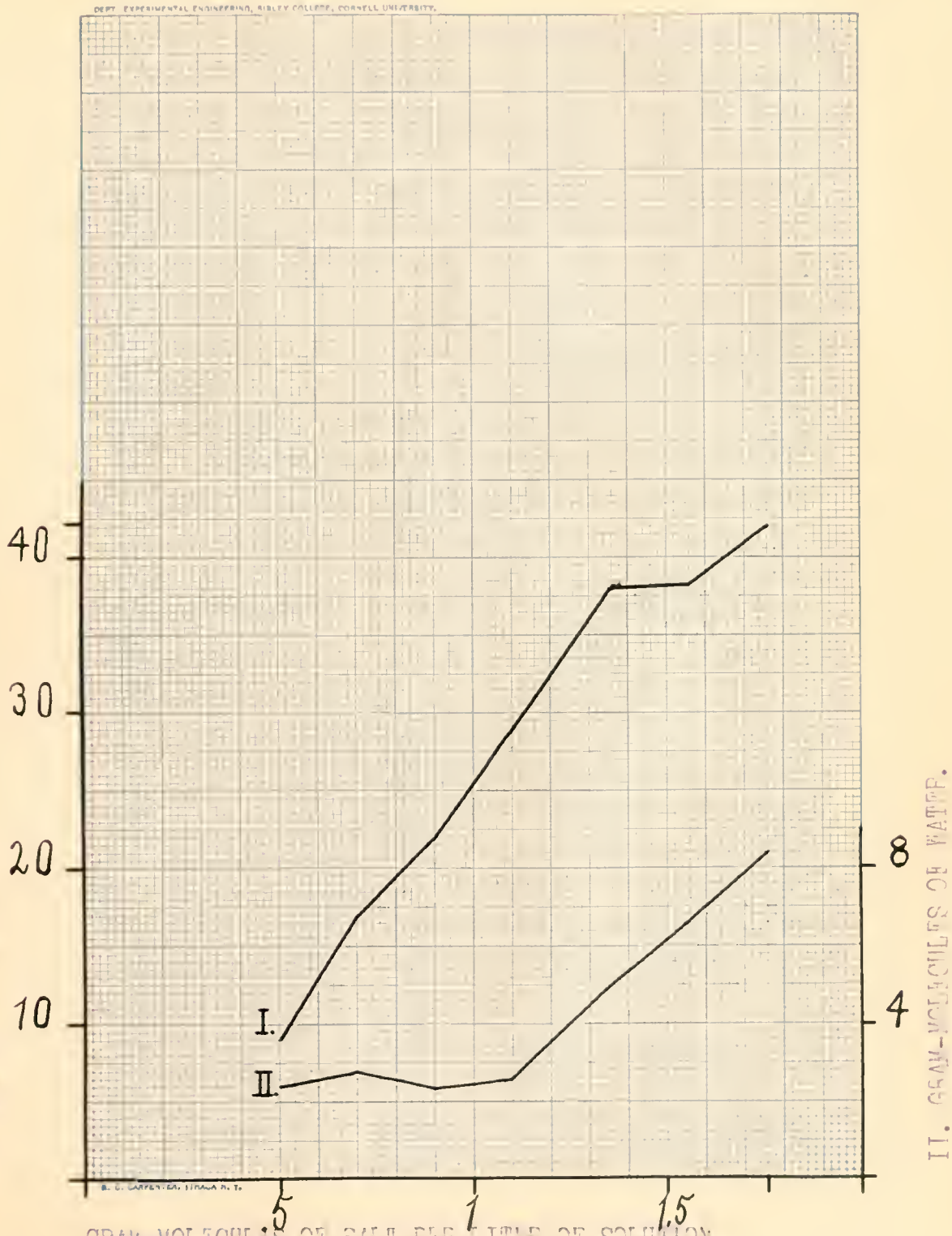


FIGURE II.

same amount of potassium chloride is added to the succeeding mixtures, the calcium chloride can increase its water of hydration only slightly, and by a constant difference, with increase in the concentration of the calcium chloride added. Consequently, there is increasing deviation in Figure I between the curve representing the value of M for the single solution and that representing M for the mixture, that is, in Figure II, the difference between the values of M for calcium chloride in the separate solution and in the mixture is approximately proportional to the difference in the amount of water present acting as solvent toward the calcium chloride in the separate solution and in the mixture. This is shown by Curve II.

It must be borne in mind that these results are based on the assumption that calcium chloride breaks down at once into $\overset{++}{Ca}$, $\overset{-}{Cl}$, $\overset{-}{Cl}$, Also, that the entire decrease in conductivity upon mixing is due to re-formation of the molecules, whereas, a part of the decrease is certainly due to viscosity and friction of the ionic spheres, as already mentioned.

In Order to Ascertain the Effect upon the Hydrates Formed, a Pair of Salts, Both of Which Have Hydrating Power, Was Next Studied.

For this purpose it was considered desirable to in-

vestigate, first, a case where both the salts employed have a large hydrating power, and where the hydrating power of the two salts in single solution is of the same order of magnitude. Calcium chloride and magnesium chloride fulfill these conditions.

CALCIUM CHLORIDE.

Table XVII. FREEZING-POINT MEASUREMENTS.

m.	Δ.	Δ/m.
0.15	0°74	4.93
0.25	1.265	5.06
0.35	1.801	5.15
0.45	2.35	5.22
0.65	3.65	5.62
0.85	5.05	5.94
1.05	6.65	6.33
1.25	8.41	6.73
1.45	10.51	7.25

Table XVIII. CONDUCTIVITY MEASUREMENTS.

Λ_∞, 0° = 147.5.

m.	v.	k.	Λ_v.	α.
0.15	6.6666	.014991	99.9	0.677
0.25	4.0000	.024077	96.3	.653
0.35	2.8571	.032700	93.4	.633
0.45	2.2222	.039688	88.2	.598
0.65	1.538	.054276	83.4	.565
0.85	1.1765	.066903	78.7	.534
1.05	0.9523	.078344	74.5	.505
1.25	0.8000	.088853	71.1	.482
1.45	0.6897	.097385	67.2	.455

Table XIX. WEIGHT-NORMAL CORRECTIONS.

m.	$W_{Sol.}$	$W_{Salt.}$	W_{H_2O}	Correction Per Cent.
0.15	25.3227	0.11625	24.90645	0.4
0.25	25.5423	.09375	24.84855	0.6
0.35	25.8040	.07125	24.83275	0.7
0.45	26.0110	1.34875	24.76225	1.0
0.65	26.4364	1.80375	24.63465	1.5
0.85	26.8816	2.35875	24.52285	1.9
1.05	27.2846	2.91375	24.37085	2.5
1.25	27.6792	3.46875	24.21045	3.2
1.45	28.1293	4.03375	24.10555	3.6

Table XX. HYDRATES.

m.	α.	L.	Δ/m.	L'.	[illegible]	H.
0.15	0.677	4.58	4.93	4.91	6.0	40.9
0.25	.653	[illegible].39	5.06	5.03	[illegible].2	32.8
0.35	.633	4.22	5.15	5.11	9.7	27.8
0.45	.598	4.08	5.22	5.17	11.7	25.9
0.65	.565	3.96	5.62	5.53	15.7	24.3
0.85	.534	3.85	5.94	5.87	18.9	22.3
1.05	.505	3.74	6.33	6.18	21.9	20.9
1.25	.482	3.65	6.76	6.50	24.3	19.5
1.45	.455	3.55	7.25	6.99	27.3	18.8

MAGNESIUM CHLORIDE.

Table XXI. FREEZING-POINT MEASUREMENTS.

m.	Δ.	Δ/m.
0.15	0°.747	4.98
0.25	1.306	5.22
0.35	1.910	5.46
0.45	2.537	5.64
0.65	3.854	5.93
0.85	5.404	6.36
1.05	7.181	6.84
1.25	9.236	7.39
1.45	11.47	7.91

Table XXII. CONDUCTIVITY MEASUREMENTS.

m.	v.	k.	Λ_v.	α.
0.15	6.6666	.013642	90.9	0.705
0.25	4.0000	.021529	86.1	.667
0.35	2.8571	.0[illegible]	80.7	.625
0.45	2.2222	.036188	80.1	.627
0.65	1.538	.047864	73.6	.570
0.85	1.1765	.057606	67.8	.525
1.05	0.9523	.066280	63.1	.486
1.25	0.8000	.073499	58.8	.456
1.45	0.6896	.078040	53.8	.417

Table XXIII. WEIGHT-NORMAL CORRECTIONS.

m.	Wsol.	Wsalt.	W_{H_2O}	Correction Per Cent.
0.15	25.2254	0.7572	24.9682	0.9
0.25	25.5072	.5954	24.9118	.4
0.35	25.7066	.8385	24.8771	.5
0.45	25.8825	1.717	24.8108	.8
0.65	26.3878	1.5480	24.6698	1.2
0.85	26.6460	2.0243	24.6217	1.5
1.05	27.0011	2.5006	24.5005	2.0
1.25	27.3538	2.9768	24.3770	2.5
1.45	27.7095	3.4532	24.2563	3.0

Table XXIV. HYDRATES.

m.	α.	L.	Δ/m.	L'.	N.	H.
0.15	0.705	4.46	4.96	4.97	5.5	76.5
0.35	.667	4.34	5.22	5.20	9.2	76.7
0.35	.625	4.19	5.16	5.43	12.7	76.7
0.45	.601	4.10	5.64	5.68	14.9	33.1
0.65	.570	3.98	5.93	5.86	17.8	27.4
0.85	.525	3.81	6.36	6.26	21.7	25.6
1.05	.489	3.68	6.84	6.70	25.1	23.9
1.25	.456	3.56	7.39	7.20	28.1	22.5
1.45	.417	3.41	7.91	7.67	30.9	21.3

MIXTURES OF CALCIUM CHLORIDE AND MAGNESIUM CHLORIDE.

Table XXV. FREEZING-POINT MEASUREMENTS.

m.	P.	Δ.
0.3 $CaCl_2$	1	1°553
0.3 $MgCl_2$	1	
0.5 $CaCl_2$ 0.5 $MgCl_2$	1 "	2.704
0.7 $CaCl_2$ 0.7 $MgCl_2$	1 "	4.053
0.9 $CaCl_2$ 0.9 $MgCl_2$	1 "	5.543
1.3 $CaCl_2$ 1.3 $MgCl_2$	1 "	9.320
1.7 $CaCl_2$ 1.7 $MgCl_2$	1 "	12.50
2.1 $CaCl_2$ 2.1 $MgCl_2$	1 "	15.50
2.5 $CaCl_2$ 2.5 $MgCl_2$	1 "	17.95
2.9 $CaCl_2$ 2.9 $MgCl_2$	1 "	17.9

TABLE XXVI. CONDUCTIVITY MEASUREMENTS.

m.	P.	m_c.	v_c.	k_u.	k.	D.	k_c.	Λ_v.	α.
0.3 $CaCl_2$	1	.15	6.6666	.026923	.014991	.001711	.014062	93.8	0.626
0.3 $MgCl_2$	1	.15	"		.013642		.012861	85.7	.664
0.5 $CaCl_2$	1	.25	4.000	.041214	.024073	.004388	.021703	86.8	.635
0.5 $MgCl_2$	1	.25	"		.021529		.019505	78.0	.605
0.7 $CaCl_2$	1	.35	2.8571	.053615	.032790	.007325	.028817	82.3	.552
0.7 $MgCl_2$	1	.35	"		.028240		.024798	70.9	.549
0.9 $CaCl_2$		.45	2.2222	.065080	.039688	.010791	.033822	75.2	.510
0.9 $MgCl_2$	1	.45	"		.036183		.031258	69.5	.533
1.3 $CaCl_2$	"	.65	1.533	.082101	.054236	.019999	.043256	66.9	.454
1.3 $MgCl_2$	1	.85	"		.047364		.038575	59.3	.460
1.7 $CaCl_2$	"	.85	1.1765	.094339	.066903	.03017	.050933	59.9	.406
1.7 $MgCl_2$	1	.85	"		.057606		.043406	51.1	.396
2.1 $CaCl_2$	"	1.05	0.9523	.10078	.078244	.04374	.055264	52.6	.357
2.1 $MgCl_2$	1	1.05	"		.063280		.04552	43.4	.336
2.5 $CaCl_2$	1	1.25	0.8000	.10273	.088853	.05957	.057913	46.3	.314
2.5 $MgCl_2$	"	1.25	"		.073400		.044869	35.9	.273
2.9 $CaCl_2$	1	1.45	0.68966	.10007	.097385	.07536	.058345	40.6	.275
2.9 $MgCl_2$	"	1.45	"		.078040		.04122	28.4	.220

Table XXVII. WEIGHT-NORMAL CORRECTIONS.

n.	P.	$W_{sol.}$	$W_{salt.}$	W_{H_2O}	Correction Per Cent.
0.3 $CaCl_2$ 0.3 $MgCl_2$	1 "	25.6480	0.77345	24.87255	0.5
0.5 $CaCl_2$ 0.5 $MgCl_2$	1 "	26.0814	1.28915	24.74225	1.0
0.7 $CaCl_2$ 0.7 $MgCl_2$	1 "	26.4594	1.80475	24.65465	1.4
0.9 $CaCl_2$ 0.9 $MgCl_2$	1 "	26.8453	2.32045	24.52485	1.9
1.3 $CaCl_2$ 1.3 $MgCl_2$	1 "	27.6088	3.35175	24.25705	3.0
1.7 $CaCl_2$ 1.7 $MgCl_2$	1 "	28.3821	4.38305	23.99905	4.0
2.1 $CaCl_2$ 2.1 $MgCl_2$	1 "	29.1096	5.41435	23.69525	5.2
2.5 $CaCl_2$ 2.5 $MgCl_2$	1 "	29.8373	6.44555	23.38775	6.5
2.9 $CaCl_2$ 2.9 $MgCl_2$	1 "	30.5280	7.47675	23.05125	7.8

In Table XXVIII, n = normal concentration of each salt in the mixture. α = dissociation of each salt in the mixture, as given in Table XXVI. mL = lowering of freezing-point, calculated from formula $[(1.86 \times 2\alpha) + 1.86]n$ The correction per cent is deduced on the assumption that the two salts form the same hydrates in the mixture that

they form in separate solutions. Upon this assumption the amount of water which each salt would eliminate from the sphere of action as solvent is calculated from the formula:— $1000 - \left[\frac{L}{L'} \times 1000\right]$. The values for magnesium chloride and calcium chloride are added together and to this is added also the difference between 1000 grams and the amount of water actually present in one liter as given by the weight-normal corrections. This, then, is given as a percentage correction in column headed Correction Per Cent. The value mL is divided by this per cent, and the result given under Table XXVIII.

m.	P.	m_c.	α.	mL.	Correction Per Cent	Δ.
0.3 $CaCl_2$	1	0.15	.636	0.634	78.9	0.803
0.3 $MgCl_2$	"		.664	0.650		0.823
0.5 $CaCl_2$	1	0.25	.589	1.012	68.0	1.488
0.5 $MgCl_2$	"		.605	1.027		1.510
0.7 $CaCl_2$	1	0.35	.558	1.378	58.8	2.345
0.7 $MgCl_2$	"		.519	1.366		2.325
0.9 $CaCl_2$	1	0.45	.510	1.690	51.2	3.298
0.9 $MgCl_2$	"		.548	1.738		3.392
1.3 $CaCl_2$	1	0.65	.454	2.36	38.5	5.998
1.3 $MgCl_2$	"		.460	2.321		6.035
1.7 $CaCl_2$	1	0.85	.406	2.865	25.8	11.13
1.7 $MgCl_2$	"		.396	2.852		11.00
2.1 $CaCl_2$	1	1.05	.357	3.346	14.7	22.85
2.1 $MgCl_2$	"		.336	3.264		22.29

Evidently the sum of the values of Δ for calcium ch-

loride and Magnesium chloride, as thus found, should equal the lowering found experimentally for the mixture in question. These values are placed side by side, for comparison, in

Table XXIX.

m.	P.	Mc.	Δ (calculated)	Δ (Exp.)	Diff.
0.3 $CaCl_2$ 0.3 $MgCl_2$	1 "	0.15 "	1°626	1.553	0.073
0.5 $CaCl_2$ 0.5 $MgCl_2$	1 "	0.25 "	2.998	2.704	0.294
0.7 $CaCl_2$ 0.7 $MgCl_2$	1 "	0.35 "	4.670	4.053	0.617
0.9 $CaCl_2$ 0.9 $MgCl_2$	1 "	0.45 "	6.690	5.543	1.147
1.3 $CaCl_2$ 1.3 $MgCl_2$	1 "	0.65 "	12.033	9.320	2.713
1.7 $CaCl_2$ 1.7 $MgCl_2$	1 "	0.85 "	22.13	13.5	8.629
2.1 $CaCl_2$ 2.1 $MgCl_2$	1 "	1.05 "	45.14	19.5	25.64

It is unnecessary to extend these calculations to the remaining more concentrated mixtures, since it is evident that the differences between the values calculated on the basis that the two salts form the same hydrates in separate solutions that they form in the mixtures, and the values

for Δ obtained experimentally, become increasingly large with increase in concentration. It is farther evident that the hypothesis is untenable from the fact that it would call for the elimination of 944 grams of water per liter of solution in the case of the 2.5 N mixture of the above salts, and for 1047 grams eliminated from the sphere of action as solvent in the case of the 2.9 N mixture.

At the moment of mixing the two solutions, each salt is prevented from forming the hydrate which it ordinarily forms in separate solution, by the amount of water which has been eliminated from the sphere of action as solvent in the formation of the hydrate of the other component of the mixture. Consequently, for the more dilute solutions at least, the hydrates formed by a salt in separate solution should be related to the hydrates formed by the same salt in the mixture at corresponding concentrations, as the amount of water present as solvent in the single solution is to the amount present as solvent in the mixture. That is, taking calcium chloride and magnesium chloride, 0.15 N solutions of each, referring to Tables XX and XXIV, if x represents the unknown value of N in the mixture; for calcium chloride, 6.0 : x :: 1000 : 897. 6.0 is the value of N for 0.15 N

calcium chloride in separate solution, and this has been corrected to 1000 grams of solvent. The figure 897 is found by subtracting from 1000 the number of grams of water with which the magnesium chloride combines when it forms the hydrate indicated for the concentration in question in Table XXIV, plus the difference between the amount of water present in the solution and 1000 grams as given by the weight-normal correction.

Having thus obtained the values of M for the salts in the mixture, it is possible to solve for L' from the equation $M = \frac{1000 - \left[\frac{L}{L'} \times 1000\right]}{18}$, where L represents the theoretical lowering found for the salt by calculating it from the value of α which has been determined for the mixture in question. This value of L' must then be corrected, in order to obtain the value as it would be observed, by dividing it by the proper per cent. This percentage correction is found by deducing the number of grams of water eliminated as water of hydration by the other salt in the mixture, basing the calculation upon the value of M worked out for the mixture. To this must be added the percentage correction which the weight-normal correction has given.

The sum of these values for L' for the two salts in the mixture should then be equal to Δ as found experimentally for the mixture, provided this hypothesis is correct. In the following table the values thus obtained are given.

M_0= the value for M deduced from the proportion.

L'_0 = " " " L' calculated upon this value of M.

$L'^{Cor.}_0$ = " " L', with proper percentage correction.

Sum = the sum of these two values for $L'^{Cor.}_0$ multiplied by the normality of the solution.

Δ = the lowering found experimentally for the same mixture.

The other symbols employed have the usual significance.

TABLE XXX.

μ.	P.	n_c.	M.	M_c.	L.	L_c'	$L_c'^{con}$.	Sum.	Δ .
0.3 $CaCl_2$	1	.15	6.0	5.4	4.224	4.682	5.16	1.57	1.552
0.3 $MgCl_2$	"	.15	5.5	4.9	4.331	4.748	5.29		
0.5 $CaCl_2$	1	.25	8.2	6.8	4.109	4.695	5.52	2.74	2.704
0.5 $MgCl_2$	"	.25	9.2	7.8	4.05	4.715	5.44		
0.7 $CaCl_2$	1	.35	9.7	7.5	3.936	4.547	5.71	3.97	4.059
0.7 $MgCl_2$	"	.35	12.7	10.5	3.902	4.808	5.64		
0.9 $CaCl_2$	1	.45	11.7	8.6	3.755	4.433	5.77	5.26	5.548
0.9 $MgCl_2$	"	.45	14.9	11.8	3.832	4.397	5.92		
1.3 $CaCl_2$	1	.65	15.7	10.7	3.548	4.394	5.94	7.74	8.32
1.3 $MgCl_2$	"	.65	17.8	12.8	3.57	4.639	5.97		
1.7 $CaCl_2$	1	.85	18.9	11.5	3.371	4.251	6.06	10.21	13.5
1.7 $MgCl_2$	"	.85	21.7	14.8	3.332	4.437	5.96		

Without further extending this method of calculation it is evident that it does not give the true value of the hydrates formed, and that the hydrating power is larger for the more concentrated mixtures than would be indicated by the proportions given above.

This is just what we should expect, for with increasing hydration we do not have the process of loss of water from the hydrates formed in separate solution going on to the end in the mixture, but instead we have, necessarily, a condition of equilibrium between the hydrating powers of the two salts. Also, as a direct result, the amount of water thus left uncombined affects the final composition of the hydrates, as already indicated.

This condition of equilibrium is not represented by the proportions given above, since the amount of water playing the part of solvent is not that indicated by these proportions.

If we consider that the values of M for calcium chloride and for magnesium chloride in separate solutions, since their hydrating powers are nearly equal, represent the relative hydrating powers under the same conditions for the two salts, at that concentration corresponding to

any pair of values of M, then it becomes possible to calculate the approximate composition of the hydrates of calcium chloride and magnesium chloride in the mixture, for, selecting for example the mixture consisting of 1 part of 1.7 N calcium chloride and 1 part of 1.7 N magnesium chloride, then:-

Let x equal the number of grams of water eliminated in formation of the hydrate of calcium chloride which occurs in the mixture in question. If the hydrates of calcium chloride and magnesium chloride in the mixture are related as they are in separate solutions, they will be to each other as 18.9 : 21.7 (see Tables XX and XXIV), hence,

$\frac{217}{189}x$ = the number of grams of water eliminated in formation of hydrate of magnesium chloride in the mixture.

From fromula, $M = \frac{1000 - \left[\frac{L}{I'} \times 1000\right]}{18}$, we have,

(1) $x = 1000 - \frac{3371}{L'_{Ca}}$, where 3.371 is the lowering found for 0.85 N calcium chloride by calculation from the value of α given in Table XXVI, and L'_{Ca} = the lowering observed for calcium chloride corrected properly for water lacking from 1000 grams, and multiplied by m.

Similarly, $\frac{217}{189}x = 1000 - \frac{5332}{L'_{Mg}}$. (2)

Let L_0' = observed lowering due to magnesium chloride. Then, $18.5 - L_0'$ = observed lowering due to calcium chloride, (vid. Table XXV).

Then, $L_0' = (L_{Mg}' \times 0.85) \div \left(1 - \frac{x}{1000} - \frac{4}{100}\right)$. (3)

where 0.85 is the normality in question, and the second parentheses is the necessary percentage correction, based upon the value of x and the correction given in Table XXVII.

Similarly, $18.5 - L_0' = (L_{Ca}' \times 0.85) \div \left(1 - \frac{217x}{1000} - \frac{4}{100}\right)$. (4)

From equation (1), $L_{Ca}' = \frac{3871}{1000 - x}$. (5)

" " (2), $L_{Mg}' = \frac{3872}{1.000 - 1.148x}$. (6)

Eliminating L_0' by combining equations (3) and (4) and then substituting the values of L_{Ca}' and L_{Mg}' from (5) and (6), it becomes possible to solve for x. By this method the values of x for calcium chloride and magnesium chloride in this mixture are found to be 17.1 and 19.6, respectively.

By the above method the values of x for the mixtures between 0.9 N and 2.9 N have been derived, and are given in the following table, under x_c. The abbreviations at the top of each column have the usual significance, the suffix c indicating that the values are for the salt in the mixture.

TABLE XXXI.

L.	P.	L_c.	α.	L_c.	M.	Δ.	Sp. Gr. Cor.	M_c.	d_c.
1.8	$CaCl_2$	1	0.65	0.454	3.549	15.74	9°32	3.0	14.5	22.9
1.8	$MgCl_2$	"	0.65	.460	3.57	17.79			16.4	25.2
1.7	$CaCl_2$	1	0.85	.406	3.371	18.92	18.5	4.0	17.1	20.1
1.7	$MgCl_2$	"	0.85	.396	3.382	21.78			19.6	23.1
2.1	$CaCl_2$	1	1.05	.357	3.187	21.92	19.5	5.2	19.3	18.9
2.1	$MgCl_2$	"	1.05	.336	3.264	25.06			22.7	21.6
2.5	$CaCl_2$	1	1.25	.314	3.028	24.32	27.25	6.5	22.3	18.2
2.5	$MgCl_2$	"	1.25	.278	2.895	28.14			26.2	21.0
2.9	$CaCl_2$	1	1.45	.275	2.883	27.29	37.0	7.8	25.9	17.9
2.9	$MgCl_2$	"	1.45	.220	2.679	30.86			28.9	19.9

MAGNESIUM CHLORIDE ALONE.
" " MIXED WITH CALCIUM CHLORIDE.
. CALCIUM CHLORIDE ALONE.
" " MIXED WITH MAGNESIUM CHLORIDE.

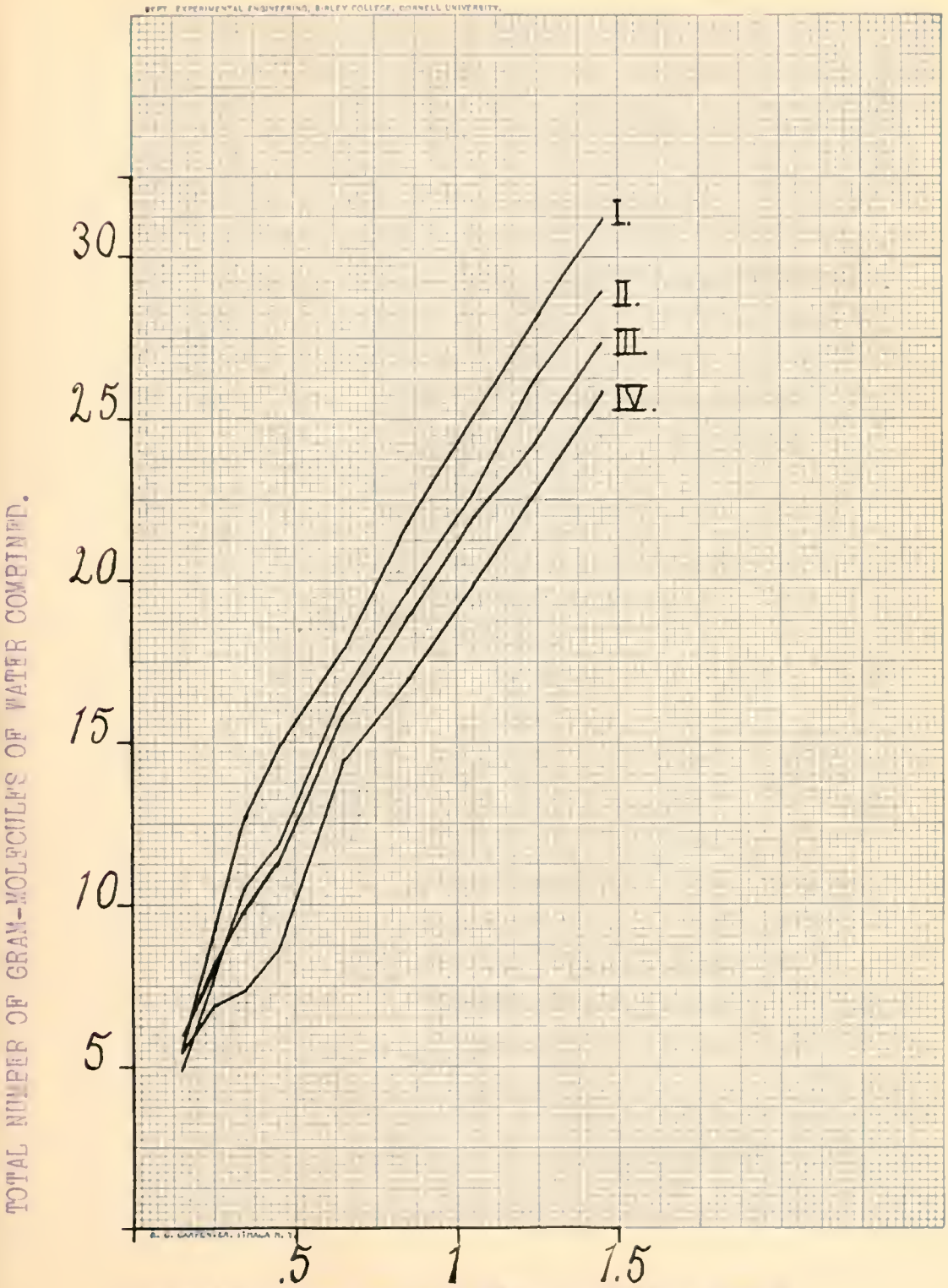


FIGURE III.

For the sake of comparison the values of M are plotted as curves for calcium chloride and magnesium chloride in separate solutions against concentration, (as axis of abscissas). Upon the same sheet are drawn similar curves for the values of M in the mixture.

Upon comparing curve I, the hydration of magnesium chloride alone, with curve IV, the hydration of the calcium chloride in the mixture, it will be seen that where I rises IV falls, and vice versa. This is exactly what we should expect, since an increase in the hydrating power of magnesium chloride should result in a corresponding decrease in the amount of water with which the calcium chloride would be able to combine in the mixture, unless a corresponding increase in the hydrating power of the calcium chloride in separate solution should also occur. Again, comparing curves I and II, and III and IV, the hydrates in separate solution and in the mixture are of the same general order of magnitude, except where the presence of the one salt in the mixture alters the composition of the hydrate formed by the other.

It was Thought Desirable to Compare the Effect of a Salt with less Hydrating Power Mixed with One of Greater Hydrating Power.

For this purpose calcium chloride and strontium chlor

ide were selected, the hydrating power of strontium chloride being somewhat less than that of calcium chloride.

The data for the separate solutions of calcium chloride has already been given. That of strontium chloride follows.

STRONTIUM CHLORIDE.

Table XXXII. FREEZING-POINT MEASUREMENTS.

m.	Δ.	Δ/m.
0.15	0°753	5.02
0.25	1.249	5.00
0.35	1.774	5.07
0.45	2.328	5.18
0.65	3.521	542
0.85	4.863	5.72
1.05	6.354	6.05
1.28541	7.861	6.56

Table XXXIII. CONDUCTIVITY MEASUREMENTS.

m.	v.	k.	Λ_v.	α.
0.15	6.6666	.015877	102.5	0.747
0.25	4.0000	.024185	96.7	.705
0.35	2.8571	.03259	93.1	.678
0.45	2.2222	.040479	90.0	.655
0.65	1.538	.055017	84.6	.616
0.85	1.1764	.067824	79.8	.581
1.05	0.9523	.079716	76.0	.553
1.28541	0.8945	.088697	71.7	.522

Table XXXIV. WEIGHT-NORMAL COMPOSITIONS.

m.	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction Per Cent.
0.15	25.5325	0.59437	24.9381	0.3
0.25	25.8496	0.9906	24.85898	0.6
0.35	26.1900	1.38688	24.8031	0.8
0.45	26.5388	1.7831	24.7557	1.0
0.65	27.1944	2.5756	24.6188	1.5
0.85	27.8553	3.3681	24.4872	2.1
1.05	28.5072	4.1606	24.4066	2.4
1.23541	29.1297	4.8954	24.2344	3.1

Table XXXV. HYDRATES.

m.	α.	L.	Δ/m.	L'.	M.	H.
0.15	0.747	4.64	5.02	4.99	3.9	26.0
0.25	.705	4.48	5.00	4.97	5.5	22.0
0.35	.678	4.39	5.07	5.05	7.1	20.3
0.45	.655	4.30	5.18	5.13	9.0	20.0
0.65	.616	4.15	5.42	5.34	12.4	19.1
0.85	.581	4.02	5.72	5.60	15.7	18.5
1.05	.553	3.92	6.05	5.91	18.7	17.8
1.23541	.522	3.80	6.36	6.17	21.3	17.2

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MIXTURE OF CALCIUM CHLORIDE AND STRONTIUM CHLORIDE.

Table XXXVI. FREEZING-POINT MEASUREMENTS.

m.	P.	Δ.
0.7 $CaCl_2$ 0.3 $SrCl_2$	1 "	1°507
0.5 $CaCl_2$ 0.5 $SrCl_2$	1 "	2.026
0.7 $CaCl_2$ 0.7 $SrCl_2$	1 "	3.906
0.9 $CaCl_2$ 0.9 $SrCl_2$	1 "	5.710
1.3 $CaCl_2$ 1.3 $SrCl_2$	1 "	8.682
1.7 $CaCl_2$ 1.7 $SrCl_2$	1 "	12.924
2.1 $CaCl_2$ 2.1 $SrCl_2$	1 "	18.29
2.5 $CaCl_2$ 2.5 $SrCl_2$	1 "	Salt separates out.

Table XXXVIII WEIGHT-NORMAL CORRECTIONS.

m.	P.	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction Per Cent.
0.5 $CaCl_2$ 0.5 $SrCl_2$	1 "	25.8463	1.0106	24.8357	0.7
0.5 $CaCl_2$ 0.5 $SrCl_2$	1 "	26.4106	1.6844	24.7262	1.1
0.7 $CaCl_2$ 0.7 $SrCl_2$	1 "	26.9452	2.3581	24.5871	1.7
0.9 $CaCl_2$ 0.9 $SrCl_2$	1 "	27.4711	3.0319	24.4392	2.2
1.3 $CaCl_2$ 1.3 $SrCl_2$	1 "	28.5671	4.3794	24.1877	3.3

TABLE XXXVII. CONDUCTIVITY MEASUREMENTS.

T.	P.	m_c.	v_c.	k_w.	k.	D.	k_c.	Λ_v	α.
0.3 $CaCl_2$	1	0.15	6.6666	.014991	.028239	.002129	.013837	92.8	0.625
0.3 $SrCl_2$	"	.15	"	.015377			.014402	96.0	.699
0.5 Ca	1	.25	4.0000	.024073	.043980	.004278	.021775	87.1	.590
0.5 Sr	"	.25	"	.024185			.022205	88.8	.647
0.7 Ca	1	.35	2.8571	.03270	.05188	.007102	.02890	82.6	.560
0.7 Sr	"	.35	"	.03259			.02929	83.7	.610
0.9 Ca	1	.45	2.2222	.039688	.070491	.009676	.034456	76.6	.519
0.9 Sr	"	.45	"	.040479			.036035	80.1	.588
1.3 Ca	1	.65	1.538	.054286	.090731	.018522	.044245	68.1	.461
1.3 Sr	"	.65	"	.055017			.046486	71.5	.521
1.7 Ca	1	.85	1.1765	.066903	.10555	.029177	.051170	60.2	.408
1.7 Sr	"	.85	"	.067824			.054389	64.0	.466
2.1 Ca	1	1.05	0.9523	.078244	.11428	.04376	.054584	52.0	.352
2.1 Sr	"	1.05	"	.079796			.059696	56.9	.414

Table XXXVIII (Cont.). WEICHI-NORMAL CORRECTIONS.

m.	P.	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction Per Cent.
1.7 $CaCl_2$ 1.7 $SrCl_2$	1 "	29.6861	5.7269	2[illegible].9112	4.4
2.1 $CaCl_2$ 2.1 $SrCl_2$	1 "	30.6744	7.0744	23.6071	5.6

For the sake of comparison, the lowerings of the freezing-point which would be obtained for the mixture of calcium chloride and strontium chloride are given in Table XXXIX, basing them upon the same method of calculation as that already given in detail for Table XXX. The symbols used have the same significance in the two tables.

It will be noted that in Table XXXIX, again, as in the case of the mixture of calcium chloride and magnesium chloride, the difference between the lowering as calculated upon the hypothesis that for the more dilute solutions at least, the hydrates formed by a salt in separate solution are related to the hydrates formed by the same salt in the mixture at corresponding concentrations, as the amount of water present as solvent in the mixture— the difference between this and the lowering found experimentally, becomes increasingly large. This has already been discussed in the preceding case.

TABLE XXXIX.

	x.	P.	x_c.	M.	M_c.	L.	L'.	$L'^{cor.}_c$.	Sum.	Δ.
0.3	Ca	1	0.15	6.0	5.6	4.136	4.65	5.00	1.543	1.506
0.3	Sr	"	"	3.9	3.5	4.461	4.76	5.32		
0.5	Ca	1	0.25	8.2	7.8	4.056	4.67	5.16	2.646	2.626
0.5	Sr	"	"	5.5	4.6	4.266	4.65	5.43		
0.7	Ca	1	0.35	9.7	8.8	3.942	4.63	5.26	3.771	3.906
0.7	Sr	"	"	7.1	5.7	4.137	4.60	5.51		
0.9	Ca	1	0.45	11.7	9.5	3.791	4.57	5.36	4.979	5.370
0.9	Sr	"	"	9.0	6.9	4.03	4.60	5.70		
1.3	Ca	1	0.65	15.7	11.7	3.576	4.53	5.56	7.465	8.682
1.3	Sr	"	"	12.4	8.5	3.797	4.48	5.92		
1.7	Ca	1	0.85	18.9	12.8	3.373	4.39	5.61	9.877	12.924
1.7	Sr	"	"	15.7	9.7	3.593	4.35	6.00		
2.1	Ca	1	1.05	21.9	13.3	3.171	4.17	5.49	11.92	13.29
2.1	Sr	"	"	18.7	10.3	3.40	4.17	5.92		

The method of calculating the composition of the hydrates existing in a mixture of two salts with about the same hydrating power, such as calcium chloride and magnesium chloride, was based upon the assumption that the values of M in their separate solutions represent the relative hydrating powers under the same conditions for the two salts in their mixtures. While this applies where the hydrates formed are of approximately the same degree of complexity, it would involve an error in the case of two salts of very differing hydrating powers, for, if the power of forming hydrates, i.e. of eliminating water from the sphere of action as solvent, differs; then, when two such substances are mixed, if a decrease in the amount of water eliminated from the sphere of action as solvent occurs, this decrease must be assigned to the two salts inversely as their values of M in separate solutions. This follows from a consideration of the fact that the salt with greater hydrating power will have, consequently, greater power of dehydrating the salt with lesser hydrating power. Therefore, the salt which has less power to unite with water must suffer the greater loss in water of hydration in the presence of the salt with stronger hydrating power.

Upon this assumption the following method of calculating the approximate composition of the hydrates in such a

mixture, has been worked out. Take the case of the mixture consisting of one volume of 0.3 N strontium chloride and one volume of 0.3 N calcium chloride:-

Let x equal the total decrease in the number of grams of water eliminated from the sphere of action as solvent, in the mixture, as compared with that eliminated in the separate solutions.

Then $\frac{39}{99}$ x = the diminution in the number of grams of water eliminated by the calcium chloride, and

$\frac{60}{99}$ x = the diminution in the number of grams of water eliminated by the strontium chloride (see Tables XX and XXXV for the values of N in separate solutions).

108.5 grams of water were eliminated by the calcium chloride as water of hydration in the 0.15 N separate solution of that salt. (See Table XX). 70.5 grams were eliminated by the strontium chloride. (See Table XXXV). Therefore,

$$108.5 - 0.39x = 1000 - \frac{4186}{L'_{Ca}}, \quad (1) \qquad \text{and}$$

$$70.5 - 0.61\,x = 1000 - \frac{4461}{L'_{Sr}}. \quad (2)$$

$$L'_{Ca} = \frac{4186}{891.5 + 0.39\,x}, \text{ and } L'_{Sr} = \frac{4461}{929.5 + 0.61x}.$$

Let L'_0 = observed lowering for calcium chloride in the mixture, then,

$$L'_0 = \frac{4186 \times 0.15}{891.5 + 0.39x} + \frac{929.5 + 0.61x}{1000}, \quad (3) \text{ and}$$

$$1.505 - L'_0 = \frac{4461 \times 0.15}{929.5 + 0.61x} \quad \frac{884.5 + 0.39x}{1000}. \quad (4)$$

Combining equations (3) and (4),

$$1.50 = \frac{4186 \times 0.15}{822 + 0.902x + .0002879x^2} + \frac{4461 \times 0.15}{822 + 0.902x + 0.0002879x^2}.$$

From this equation the approximate value of x can be obtained. The values of N and H for the mixture of calcium chloride and strontium chloride, thus obtained, are given in Table XL. The symbols have the usual significance.

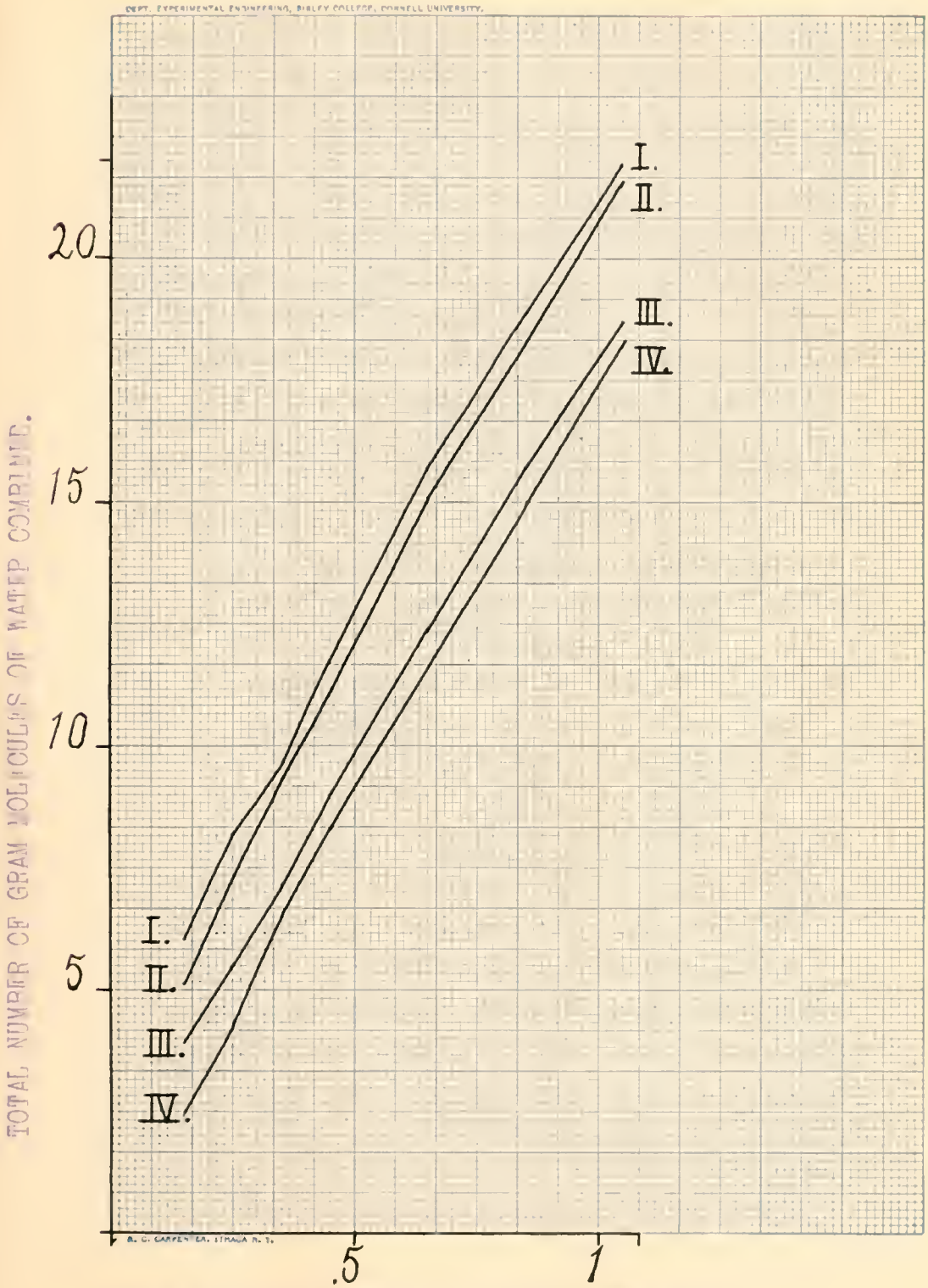
Table XL.

m.	P.	m_c.	α.	L_c.	M.	Δ.	Sp. Gr. cor.	N_c.	H_c.
0.5 $CaCl_2$	1	0.15	0.625	4.186	6.0	1.503	0.7	5.1	34.0
0.5 $SrCl_2$	"	"	.699	4.461	3.9			2.4	16.0
0.5 Ca	1	0.25	.590	4.056	8.2	2.626	1.1	7.3	29.2
0.5 Sr	"	"	.647	4.266	5.5			4.2	16.8
0.7 Ca	1	0.35	.560	3.942	9.7	3.906	1.6	9.3	26.1
0.7 Sr	"	"	.610	4.127	7.1			6.5	18.6
0.9 Ca	1	0.45	.519	3.791	11.7	5.310	2.2	11.1	24.7
0.9 Sr	"	"	.583	4.03	9.0			8.3	18.2
1.3 Ca	1	0.65	.461	3.576	15.7	8.682	3.3	15.1	23.2
1.3 Sr	"	"	.521	3.797	12.4			11.6	17.8
2.7 Ca	1	0.85	.408	3.378	18.9	12.924	4.4	18.3	21.5
2.7 Sr	"	"	.466	3.593	15.7			15.0	17.6
3.1 Ca	1	1.05	.352	3.171	21.9	18.29	5.6	21.5	20.5
3.1 Sr	"	"	.414	3.40	18.7			18.2	17.3

For the sake of comparison, the values of h for the separate solutions of calcium chloride and strontium chloride, and those in the mixture of the two salts, have been plotted in curves in Figure IV.

We find that the results expressed in Figure IV are of the same character as those shown in Figure III, for the mixture of calcium chloride and magnesium chloride. The curve of hydration of each salt in the mixture is parallel to the curve of its hydration in the single solution, except where large values are shown in Curve I, for calcium chloride alone, have produced a corresponding lessening in the amount of water which the strontium chloride has been able to unite with, in the mixture, at a normality of 0.15 to 0.35. An increase in the hydrating power of the calcium chloride must necessarily be accompanied by a corresponding decrease in the complexity of the hydrates of strontium chloride.

CALCIUM CHLORIDE ALONE.
" " MIXED WITH STRONTIUM CHLORIDE.
STRONTIUM CHLORIDE ALONE.
" " MIXED WITH CALCIUM CHLORIDE.



GRAM-MOLECULES OF SALT PER LITER IN SOLUTION.

FIGURE IV.

In order to compare the difference in the amount of water present as solvent in the single solution, and in the mixture with the difference in the value of M in the two cases; these values are tabulated. D_{H_2O} is the difference in the amount of water present as solvent in the separate solution and in the mixture. It is found for a given salt by adding to the number of grams of water eliminated as water of hydration by the other salt in the mixture, the difference between the correction to weight-normal standard in the case of the separate solution of the salt in question, and in the mixture. D_M is the difference between the value of M in th single solution and in the mixture.

Table XLI. CALCIUM CHLORIDE IN THE MIXTURE OF CALCIUM CHLORIDE AND STRONTIUM CHLORIDE.

m.	D_{H_2O}.	D_M.
0.15	46	0.9
0.25	81	0.9
0.35	127	0.4
0.45	162	0.6
0.65	226	0.6
0.85	295	0.6
1.05	359	0.4

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Table XLII. STRONTIUM CHLORIDE IN MIXTURE OF CALCIUM CHLORIDE AND STRONTIUM CHLORIDE.

m.	D_{H_2O}.	D_m.
0.15	96	1.5
0.25	137	1.3
0.35	176	0.6
0.45	212	0.7
0.65	289	0.8
0.85	353	0.7
1.05	419	5

These values are plotted in curves in Figures V and VI. The concentrations are the abscissas, and for curve I the grams of water are taken for ordinates. In curve II gram-molecules of water form the ordinates.

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DIFFERENCE BETWEEN THE VALUES OF V FOR CALCIUM CHLORIDE IN SINGLE SOLUTION AND IN THE MIXTURE OF CALCIUM CHLORIDE AND STRONTIUM CHLORIDE.

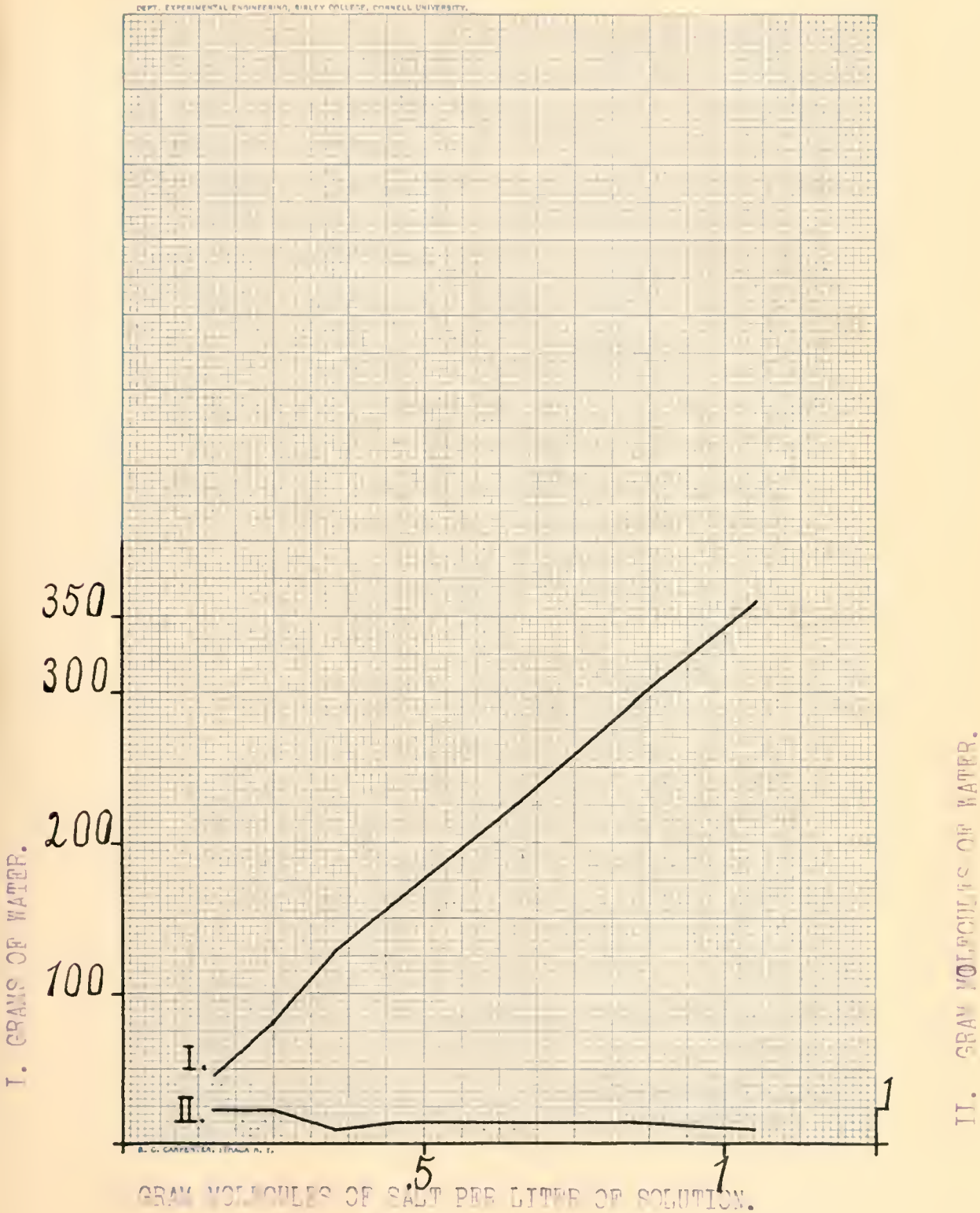

FIGURE V.

DIFFERENCE BETWEEN WATER PRESENT AS SOLVENT IN SINGLE SOLUTION OF STRONTIUM CHLORIDE AND IN MIXTURE OF CALCIUM CHLORIDE AND STRONTIUM CHLORIDE.
DIFFERENCE BETWEEN THE VALUES OF N FOR STRONTIUM CHLORIDE IN SINGLE SOLUTION AND IN THE MIXTURE OF CALCIUM CHLORIDE AND STRONTIUM CHLORIDE.

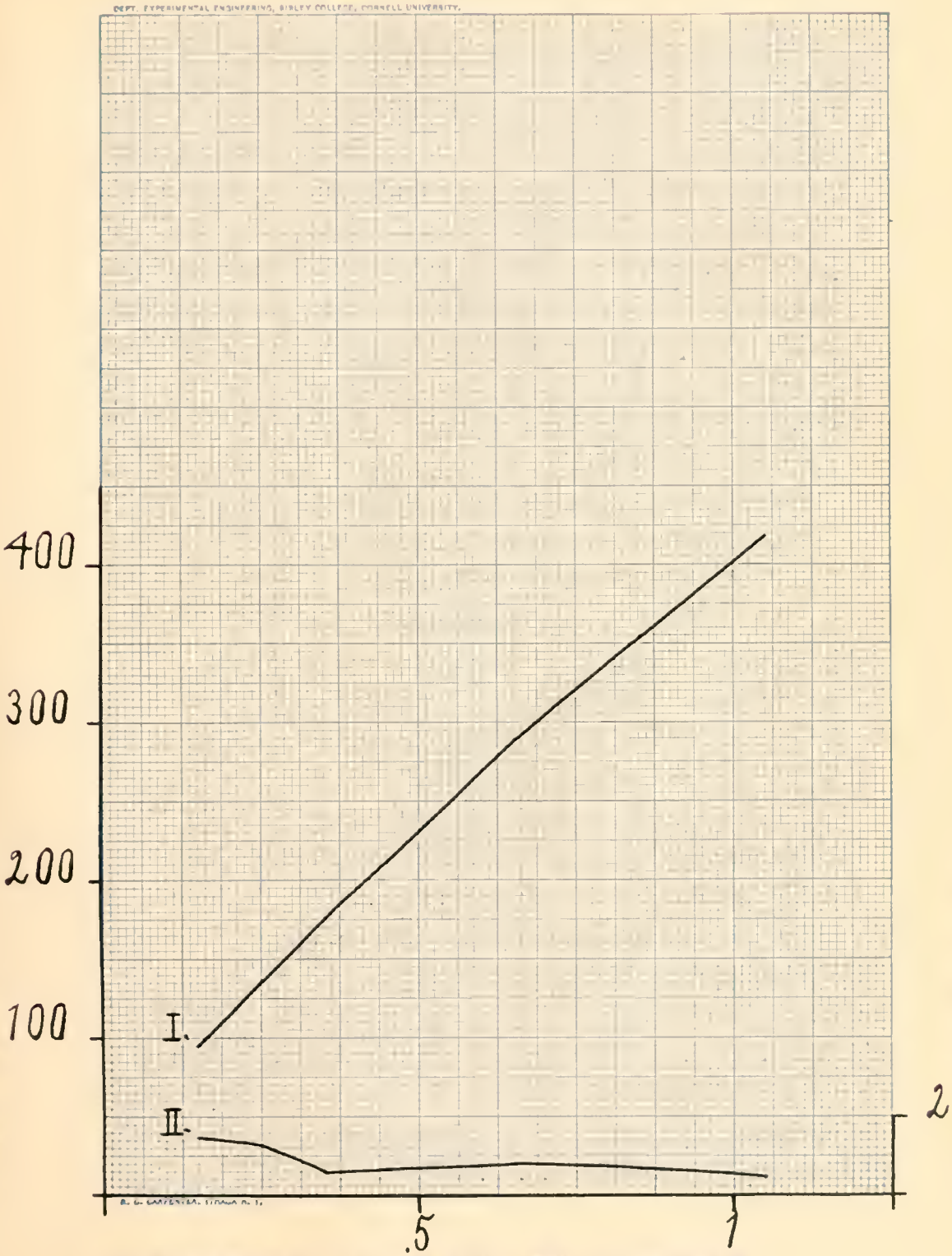

PLATE VI.

It is readily seen from a comparison of the curves that the decrease in the amount of water present as solvent in the mixture, is not accompanied by a corresponding decrease in the values of M. Here again, as in the case of the mixture of calcium chloride and potassium chloride, the difference in the values of M is nearly constant, because the concentration of both salts present in the mixture is increased at the same rate. Slight changes might be manifest if the ions and molecules have different hydrating powers, as seems very probable. Then a decrease in the number of ions and a correspondingly large increase in the number of molecules of dissolved substance present, such as necessarily occurs owing to suppression of the ionization in the mixture, would be accompanied by a change in the number of grams of water combined. That this plays a part in the change noted seems very probable.

For purposes of comparison these same values are given for a few concentrations in the case of calcium chloride and magnesium chloride. The phenomena are of the same kind.

Table XLIII. CALCIUM CHLORIDE IN CALCIUM CHLORIDE AND MAGNESIUM CHLORIDE MIXTURE.

m.	D_{H_2O}.	D_M.
0.65	310.2	1.2
0.85	373.8	1.8
1.05	435.0	2.1
1.25	507.0	1.5
1.45	562.2	1.4

Table XLIV. MAGNESIUM CHLORIDE IN CALCIUM CHLORIDE AND MAGNESIUM CHLORIDE MIXTURE.

m.	D_{H_2O}.	D_M.
0.05	279	1.4
0.85	333	2.1
1.05	389	2.4
1.25	450	1.8
1.45	514	2.0

A Pair Of Nitrates Was Next Studied.

The salts must be of such a nature as not to unite to form complexes when mixed, and must have hydrating power. Magnesium nitrate and strontium nitrate were selected. The data for these two salts follows.

MAGNESIUM NITRATE.

Table XLV. FREEZING-POINT MEASUREMENTS.

m.	Δ.	Δ/m.
0.15	0°749	4.99
0.25	1.252	5.01
0.35	1.805	5.16
0.45	2.395	5.32
0.55	3.019	5.49
0.65	3.669	5.64
0.75	4.393	5.86

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Table XLVI. CONDUCTIVITY MEASUREMENTS.

Λ_{∞}, 0°, = 128.5.

m.	v.	k.	Λ_v.	α.
0.15	6.6666	.015701	91.3	0.711
0.25	4.0000	.021563	86.3	.671
0.35	2.8571	.028613	81.8	.636
0.45	2.2222	.035123	78.1	.607
0.55	1.8182	.041506	75.5	.587
0.65	1.538	.046942	73.2	.562
0.75	1.4333	.052260	69.7	.542

Table XLVII. WEIGHT-NORMAL CORRECTIONS.

m.	$W_{Sol.}$	$W_{Salt.}$	W_{H_2O}.	Correction Per Cent.
0.15	25.4306	0.5567	24.8738	0.5
0.25	25.688	0.9277	24.7603	1.0
0.35	25.9782	1.2989	24.6794	1.3
0.45	26.2275	1.6610	24.5876	1.8
0.55	26.4748	2.0411	24.4338	2.3
0.65	26.7605	2.4122	24.3484	2.6
0.75	27.0203	2.7885	24.2371	3.1

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Table XLVIII. HYDRATES.

m.	α.	L.	Δ/m.	L'.	M.	H.
0.15	0.711	4.50	4.99	4.97	3.8	35.1
0.25	.671	4.36	5.01	4.96	6.7	26.9
0.35	.636	4.23	5.16	5.09	9.4	26.8
0.45	.607	4.12	5.32	5.22	11.7	26.0
0.55	.587	4.05	5.49	5.36	13.6	24.7
0.65	.562	3.95	5.68	5.49	15.6	24.0
0.75	.542	3.88	5.86	5.68	17.6	23.5

STRONTIUM NITRATE.

Table XLIX. FREEZING-POINT MEASUREMENTS.

m.	Δ.	Δ/m.
0.15	0°.674	4.49
0.25	1.085	4.34
0.35	1.516	4.33
0.45	1.903	4.23
0.55	2.286	4.16
0.65	2.681	4.12
0.75	3.060	4.08

Table L. CONDUCTIVITY MEASUREMENTS.

Λ_∞, 0° = 134.4.

m.	v.	k.	Λ_v.	α.
0.15	6.6666	.013164	87.8	0.653
0.25	4.0000	.019905	79.6	.592
0.35	2.8571	.025748	73.6	.548
0.45	2.2222	.030645	68.1	.507
0.55	1.8182	.035106	63.8	.475
0.65	1.538	.038986	59.9	.446
0.75	1.3333	.042076	56.1	.417

Table II. WEIGHT-NORMAL CORRECTIONS.

m.	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction Per Cent.
0.15	25.6245	0.7938	24.8307	0.7
0.25	26.0440	1.3512	24.6928	1.2
0.35	26.4408	1.8960	24.5449	1.8
0.45	26.8623	2.4376	24.4247	2.3
0.55	27.289	2.9793	24.3097	2.8
0.65	27.6907	3.5210	24.1697	3.3
0.75	28.0818	4.0627	24.0191	3.9

Table LII. HYDRATES.

m.	α.	L.	Δ/m.	L'.	M.	H.
0.15	0.653	4.29	4.49	4.46	2.1	14.1
0.25	.592	4.06	4.34	4.29	2.98	11.9
0.35	.548	3.80	4.33	4.25	4.6	13.2
0.45	.507	3.75	4.23	4.13	5.1	11.[illegible]
0.55	.475	3.68	4.16	4.04	5.6	10.3
0.65	.446	3.52	4.13	3.98	6.4	9.9
0.75	.417	3.41	4.08	3.92	7.2	9.6

The data for the mixture of magnesium nitrate and strontium nitrate follows.

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Table LIII. FREEZING-POINT MEASUREMENTS.

m.	P.	Δ.
0.3 $Mg(NO_3)_2$ 0.3 $Sr(NO_3)_2$	1 "	1°.394
0.5 $Mg(NO_3)_2$ 0.5 $Sr(NO_3)_2$	1 "	2.851
0.7 $Mg(NO_3)_2$ 0.7 $Sr(NO_3)_2$	1 "	3.571
0.9 $Mg(NO_3)_2$ 0.9 $Sr(NO_3)_2$	1 "	4.573
1.1 $Mg(NO_3)_2$ 1.1 $Sr(NO_3)_2$	1 "	5.646
1.3 $Mg(NO_3)_2$ 1.3 $Sr(NO_3)_2$	1 "	6.893
1.5 $Mg(NO_3)_2$ 1.5 $Sr(NO_3)_2$	1 "	8.109

Table LIV. WEIGHT-NORMAL CORRECTIONS.

m.	P.	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction Per Cent.
0.3 $Mg(NO_3)_2$ 0.3 $Sr(NO_3)_2$	1 "	26.044	1.3505	24.6936	1.3
0.5 $Mg(NO_3)_2$ 0.5 $Sr(NO_3)_2$	1 "	26.7087	2.3819	24.4268	2.3
0.7 $Mg(NO_3)_2$ 0.7 $Sr(NO_3)_2$	1 "	27.3970	3.1948	24.2022	3.2
0.9 $Mg(NO_3)_2$ 0.9 $Sr(NO_3)_2$	1 "	28.0570	4.1076	23.9495	4.2
1.1 $Mg(NO_3)_2$ 1.1 $Sr(NO_3)_2$	1 "	28.6884	5.0308	23.6681	5.7
1.3 $Mg(NO_3)_2$ 1.3 $Sr(NO_3)_2$	1 "	29.3508	5.9332	23.4177	6.3
1.5 $Mg(NO_3)_2$ 1.5 $Sr(NO_3)_2$	1 "	29.9912	[illegible]	23.1452	7.4

Table LIV. CONDUCTIVITY MEASUREMENTS.

n.	P.	m_c.	v_c.	k_w.	k.	D.	k_c.	Λ_∞	α.
0.3 $MgNO_3$	1	0.15	6.6666	.025242	.013701	.003025	.012288	81.9	0.648
" $Sr(NO_3)_2$	"	"	"		.018164		.011555	77.0	.573
0.5 Mg	1	0.25	4.0000	.035522	.021563	.005946	.016848	75.4	.537
0.5 Sr	"	"	"		.019905		.016681	66.7	.497
0.7 Mg	1	0.35	2.8571	.044660	.028613	.009701	.024261	69.2	.539
0.7 Sr	"	"	"		.025748		.020429	58.4	.434
0.9 Mg	1	0.45	2.2222	.051704	.035123	.014004	.028881	64.2	.500
0.9 Sr	"	"	"		.030645		.022829	50.7	.378
1.1 Mg	1	0.55	1.8182	.057068	.041506	.019526	.032987	60.0	.467
1.1 Sr	"	"	"		.035106		.024096	43.8	.326
1.3 Mg	1	0.65	1.538	.060997	.046942	.024881	.036202	55.7	.443
1.3 Sr	"	"	"		.038936		.024786	38.1	.284
1.5 Mg	1	0.75	1.3333	.063788	.052260	.030548	.03971	52.4	.408
1.5 Sr	"	"	"		.042076		.024476	32.6	.243

Table LVI. HYDRATES.

m.	P.	m_c.	α.	L_c.	M.	Δ.	Sp. Gr. Cor.	M_c.	M_c.
0.3 $Mg2NO_3$	1	0.15	0.638	4.281	5.3	1.394	1.2	4.9	32.5
0.3 $Sr2NO_3$	"	"	.573	3.992	2.1			1.0	6.6
0.5 Mg	1	0.25	.587	4.042	6.7	2.351	2.[illegible]	6.5	26.0
0.5 Sr	"	"	.497	3.707	3.0			2.4	9.6
0.7 Mg	1	0.35	.539	3.864	9.4	3.371	3.2	8.8	25.1
0.7 Sr	"	"	.434	3.476	4.6			3.4	9.6
0.9 Mg	1	0.45	.500	3.718	11.7	4.513	4.2	11.4	25.[illegible]
0.9 Sr	"	"	.378	3.264	5.1			4.4	9.8
1.1 Mg	1	0.55	.467	3.596	13.6	5.646	5.3	13.3	24.2
1.1 Sr	"	"	.326	3.073	5.6			4.9	8.8
1.3 Mg	1	0.65	.433	3.472	15.6	6.892	6.3	15.3	23.4
1.3 Sr	"	"	.284	2.915	6.4			5.5	8.5
1.5 Mg	1	0.75	.408	3.377	17.6	8.169	7.4	17.0	22.7
1.5 Sr	"	"	.243	2.763	7.2			5.7	7.6

The values of M for this mixture are calculated by the method given on pages 41,[illegible]. Evidently, the same method of calculation applies here as in the case of a mixture of calcium chloride and strontium chloride.

Table LVI.

m.	P.	m.	.	L.	M.
0.3 $MgZnO$	1	0.15	0.638	4.231	5.3
0.3 $SrZnO$	"	"	.573	3.992	2.1
0.5 Mg	1	0.25	.587	4.042	6.7
0.5 Sr	"	"	.497	3.707	3.0
0.7 Mg	1	0.35	.539	3.864	9.4
0.7 Sr	"	"	.434	3.476	4.6
0.9 Mg	1	0.45	.500	3.718	11.7
0.9 Sr	"	"	.378	3.264	5.1
1.1 Mg	1	0.55	.467	3.506	18.6
1.1 Sr	"	"	.326	3.073	5.6
1.3 Mg	1	0.65	.433	3.473	15.6
1.3 Sr	"	"	.284	2.915	6.4
1.5 Mg	1	0.75	.408	3.377	17.6
1.5 Sr	"	"	.243	2.763	7.3

The values of M in single solution and in the mixture, for magnesium nitrate and strontium nitrate, have been plotted in curves in Figure VII. The phenomena are, in general, the same as those already pointed out in preceding cases. Curve IV deviates from Curve III with increasing concentration, showing the effect of the large increase in the value of M for magnesium nitrate with increasing concentration, upon the amount of water eliminated as water of hydration by the strontium nitrate. The strontium nitrate is dehydrated, partially, by the magnesium nitrate.

MAGNESIUM NITRATE ALONE.
" " MIXED WITH STRONTIUM NITRATE.
I. STRONTIUM NITRATE ALONE.
" " MIXED WITH MAGNESIUM NITRATE.

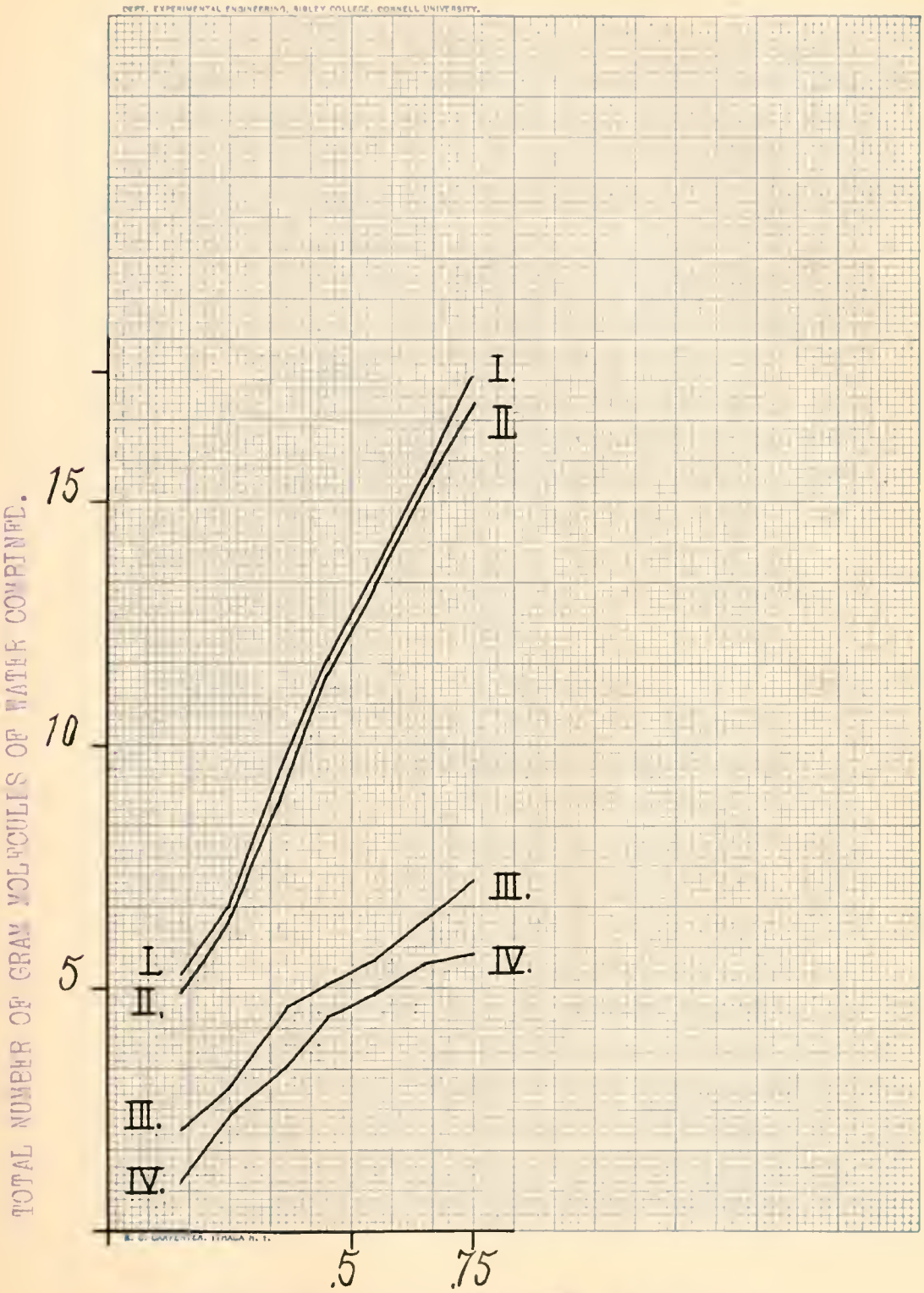


FIGURE VII.

In Tables LVII and LVIII, we have the differences in the amount of solvent present and in the values of M, as previously described for the corresponding tables.

Table LVII. MAGNESIUM NITRATE IN MIXTURE OF MAGNESIUM NITRATE AND STRONTIUM NITRATE.

m.	D_{H_2O}.	D_M.
0.15	25	0.4
0.25	56	0.3
0.35	80	0.6
0.45	108	0.5
0.55	118	0.8
0.65	136	0.4
0.75	146	0.6

Table LVIII. STRONTIUM NITRATE IN MIXTURE OF MAGNESIUM NITRATE AND STRONTIUM NITRATE.

m.	D_{H_2O}.	D_M.
0.15	93	1.1
0.25	128	0.6
0.35	172	1.5
0.45	224	0.7
0.55	264	0.7
0.65	304	0.9
0.75	341	1.5

In Figures VII and IX these values are plotted in curves.

DIFFERENCE BETWEEN WATER PRESENT AS SOLVENT IN THE SINGLE SOLUTION OF MAGNESIUM NITRATE AND IN MIXTURE OF MAGNESIUM NITRATE AND STRONTIUM NITRATE.
DIFFERENCE BETWEEN VALUES OF M FOR MAGNESIUM NITRATE IN SINGLE SOLUTION AND IN THE MIXTURE OF MAGNESIUM NITRATE AND STRONTIUM NITRATE.

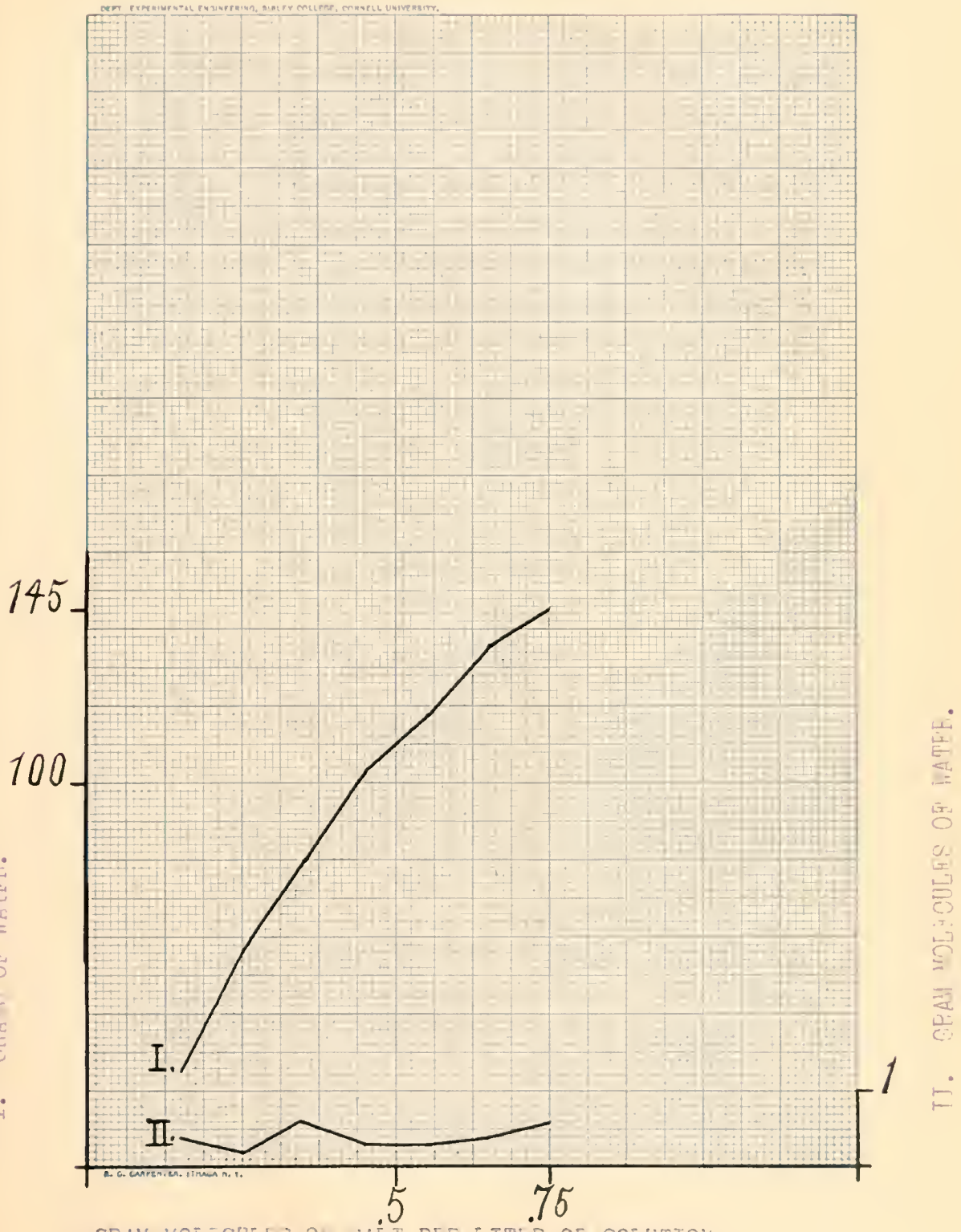
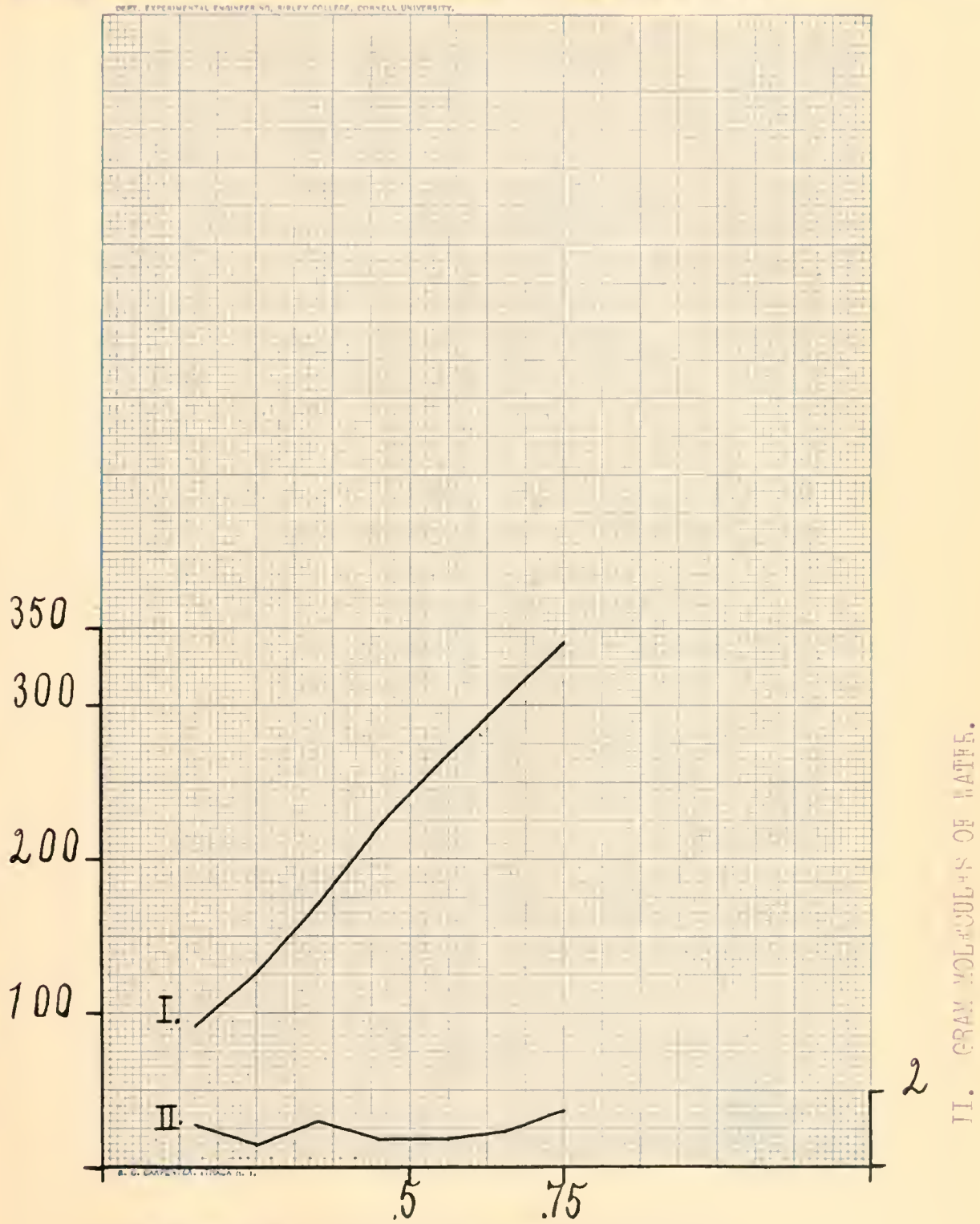


FIGURE VIII.

DIFFERENCE BETWEEN THE AMOUNT OF WATER PRESENT AS SOLVENT IN THE SINGLE SOLUTION OF STRONTIUM NITRATE AND IN THE MIXTURE OF MAGNESIUM NITRATE AND STRONTIUM NITRATE.

DIFFERENCE BETWEEN THE VALUES OF M FOR STRONTIUM NITRATE IN SINGLE SOLUTION AND IN THE MIXTURE OF MAGNESIUM NITRATE AND STRONTIUM NITRATE.



GRAM MOLECULES OF SALT PER LITER OF SOLUTION.

FIGURE IX.

We have here, again, a uniform decrease in the amount of water present as solvent, showing a uniform increase in the hydration with increase in concentration. The curves showing the differences in the values of M correspond to a constant difference in the amount of water eliminated in single solution and in the mixture. This constant difference is, of course, due to the fact that the concentration of both salts in the mixture is increased uniformly. The curves show, also, that this difference is slightly affected by the difference in the amount of water present as solvent, since they show a tendency to increase as the diminution in water present as solvent becomes greater.

We next took up a Pair of Binary Electrolytes, LITHIUM BROMIDE and SODIUM BROMIDE, Neither of Which has a very large Hydrating Power, the Hydrating Power of the Sodium Bromide being somewhat less than that of the Lithium Bromide.

SODIUM BROMIDE.

Table LIX. FREEZING-POINT MEASUREMENTS.

m.	Δ.	Δ/m.
0.35	0°895	3.58
0.35	1.249	3.57
0.45	1.601	3.56
0.55	1.946	3.54
0.65	2.298	3.54
0.75	2.691	3.59
0.85	3.054	3.59
0.95	[illegible].485	3.63

[illegible]

[illegible]

[illegible]

Table LX. CONDUCTIVITY MEASUREMENTS.

Λ_{∞}, 0°, = 67.7.

m.	v.	k.	Λ_v.	α.
0.35	4.0000	.014608	57.2	0.845
0.35	2.8571	.019628	56.1	.828
0.45	2.2222	.024848	55.2	.815
0.55	1.8182	.029744	54.1	.799
0.65	1.538	.034269	52.7	.779
0.75	1.3333	.039324	52.4	.774
0.85	1.1765	.044009	51.8	.765
0.95	1.0526	.048853	51.4	.760
1.05	0.9523	.053228	50.7	.747

Table LXI. WEIGHT-NORMAL CORRECTIONS.

m.	$W_{sol.}$	$W_{salt.}$	W_{H_2O}.	Correction Per Cent.
0.35	25.4629	0.6438	24.8191	0.4
0.35	25.7000	0.9014	24.7987	0.8
0.45	25.8823	1.1569	24.7254	1.1
0.55	26.0735	1.4164	24.6571	1.4
0.65	26.2500	1.6726	24.5874	1.7
0.75	26.4545	1.9314	24.5221	1.9
0.85	26.6155	2.1890	24.4265	2.3
0.95	26.8200	2.4405	24.3795	2.5
1.05	27.0078	2.7040	24.3038	2.8

[illegible]

[illegible]

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
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[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

Table LVII. HYDRATES.

m.	α.	L.	Δ/m.	L'.	M.	N.
0.25	0.845	3.47	3.58	3.55	1.9	7.0
0.35	.828	3.40	3.57	3.54	2.2	6.8
0.45	.815	3.38	3.56	3.52	2.2	4.9
0.55	.799	3.35	3.54	3.49	2.2	4.0
0.65	.779	3.31	3.54	3.48	2.7	4.2
0.75	.774	3.30	3.59	3.52	3.5	4.6
0.85	.765	3.28	3.59	3.51	3.6	4.2
0.95	.760	3.27	3.62	3.53	4.1	4.3
1.05	.747	3.25	3.66	3.56	4.8	4.6

LITHIUM BROMIDE.

Table LVIII. FREEZING-POINT MEASUREMENTS.

m.	Δ.	Δ/m.
0.25	0°917	3.67
0.35	1.292	3.69
0.45	1.679	3.75
0.55	2.020	3.80
0.65	2.514	3.87
0.75	2.957	3.94
0.85	3.418	4.02
0.95	3.900	4.11
1.05	4.381	4.17

Table LXIV. CONDUCTIVITY MEASUREMENTS.

m.	v.	k.	Λ_v.	α.
0.35	4.0000	.012099	50.8	0.848
0.35	2.8571	.017388	49.4	.825
0.45	2.2222	.021694	48.2	.805
0.55	1.8182	.025855	47.0	.785
0.65	1.538	.029868	45.9	.757
0.75	1.3333	.033996	45.8	.745
0.85	1.1765	.037904	44.6	.734
0.95	1.0526	.04176	44.0	.723
1.05	0.9523	.045505	43.3	

Table LXV. WEIGHT-NORMAL CORRECTIONS.

m.	$W_{Sol.}$	$W_{Salt.}$	W_{H_2O}.	Correction Per Cent.
0.35	25.3918	0.5457	24.8470	0.6
0.35	25.5641	0.7612	24.8029	0.8
0.45	25.7225	0.9786	24.7439	1.0
0.55	25.8690	1.1961	24.6729	1.3
0.65	26.0058	1.4136	24.5922	1.5
0.75	26.1385	1.6311	24.5274	1.9
0.85	26.3303	1.8485	24.4818	2.1
0.95	26.4558	2.0660	24.3898	2.4
1.05	26.6235	2.2835	24.3400	2.6

Table LVII. HYDRATES.

m.	α.	L.	Δ/m.	L'.	M.	N.
0.25	0.848	3.44	3.67	3.65	5.2	10.8
0.35	.825	3.39	3.69	3.68	5.7	10.6
0.45	.805	3.36	3.75	3.71	6.3	11.0
0.55	.785	3.32	3.80	3.75	6.8	11.0
0.65	.767	3.29	3.87	3.81	7.5	11.5
0.75	.757	3.27	3.94	3.87	8.6	11.5
0.85	.745	3.25	4.02	3.94	9.7	11.4
0.95	.734	3.23	4.11	4.01	10.8	11.4
1.05	.723	3.21	4.17	4.06	11.6	11.0

MIXTURE OF LITHIUM BROMIDE AND SODIUM BROMIDE.

Table LVII. FREEZING-POINT MEASUREMENTS.

m.	P.	Δ.
0.5 LiBr 0.5 NaBr	1 "	1°833
0.7 LiBr 0.7 NaBr	1 "	2.596
0.9 LiBr 0.9 NaBr	1 "	3.415
1.1 LiBr 1.1 NaBr	1 "	4.325
1.3 LiBr 1.3 NaBr	1 "	5.284
1.5 LiBr 1.5 NaBr	1 "	6.297
1.7 LiBr 1.7 NaBr	1 "	7.328
1.9 LiBr 1.9 NaBr	1 "	8.399
2.1 LiBr 2.1 NaBr	1 "	9.589

Table LXVIII. CONDUCTIVITY MEASUREMENTS.

m.	P.	m_c.	v_c.	k_w	k.	D.	k_c.	Λ_v.	α.
0.5 LiBr	1	0.25	4.0000	.035489	.012699	.001518	.011986	47.9	0.850
0.5 NaBr	"	"	"		.014308		.013503	54.0	.798
0.7 Li	1	0.35	2.8571	.034327	.017288	.002589	.016073	45.9	.767
0.7 Na	"	"	"		.019628		.018254	52.2	.770
0.9 Li	1	0.45	2.2222	.042737	.021694	.003810	.019905	44.2	.738
0.9 Na	"	"	"		.024843		.022882	50.7	.749
1.1 Li	1	0.55	1.8182	.051105	.025855	.004194	.023745	43.2	.721
1.1 Na	"	"	"		.029744		.027360	49.8	.735
1.3 Li	1	0.65	1.538	.058945	.029863	.005187	.027248	42.2	.704
1.3 Na	"	"	"		.034269		.031517	48.5	.716
1.5 Li	1	0.75	1.3333	.066486	.037904*	.006834	.030789	41.1	.685
1.5 Na	"	"	"		.044009		.035698	47.6	.705
1.7 Li	1	0.85	1.1765	.073132	.04176	.008781	.037841	39.8	.665
1.7 Na	"	"	"		.048853		.039391	46.2	.653
1.9 Li	1	0.95	1.0526	.080414	.045505	.010199	.03688	38.8	.648
1.9 Na	"	"	"		.053228		.043531	45.8	.677
2.1 Li	1	1.05	0.9523	.086647	.033996*	.012080	.039822	37.9	.64[illegible]
2.1 Na	"	"	"		.039324		.046815	44.6	.659

1

Since lithium bromide and sodium bromide are each binary, and dissociated to almost exactly the same extent at equal concentrations of the solutions, the loss in conductivity is apportioned to an equal driving back in the dissociation of the lithium bromide and sodium bromide, except in the mixtures $\left.\begin{matrix}1.7\ LiBr\\1.7\ NaBr\end{matrix}\right\}$ and $\left.\begin{matrix}1.9\ LiBr\\1.9\ NaBr\end{matrix}\right\}$, where the slight difference in the dissociation of the separate solutions is taken into account.

Table LXIX. WEIGHT-NORMAL CORRECTIONS.

m.	P.	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction Per Cent.
0.5 LiBr 0.5 NaBr	1 "	25.9003	1.18748	24.7128	1.1
0.7 LiBr 0.7 NaBr	1 "	26.2462	1.6625	24.5837	1.7
0.9 LiBr 0.9 NaBr	1 "	26.6053	2.1375	24.4678	2.1
1.1 LiBr 1.1 NaBr	1 "	26.9317	2.6125	24.3192	2.7
1.3 LiBr 1.3 NaBr	1 "	27.2984	3.0875	24.2121	3.2
1.5 LiBr 1.5 NaBr	1 "	27.5978	3.5625	24.0353	3.9
1.7 LiBr 1.7 NaBr	1 "	27.9400	4.0375	23.9025	4.4
1.9 LiBr 1.9 NaBr	1 "	28.2890	4.5125	23.7765	4.9
2.1 LiBr 2.1 NaBr	1 "	28.6065	4.9875	23.6190	5.5

The values of W and H for this mixture are calculated

Table LXX. HYDRATES.

m.	P.	m_c.	α.	L_c.	M.	Δ.	Sp. Gr. Cor.	M_c.	H_c.
0.5 LiBr	1	0.25	0.800	3.349	3.2	1.823	1.1	2.8	11.2
0.5 NaBr	"	"	.798	3.344	1.9			1.2	4.8
0.7 Li	1	0.35	.767	3.286	3.7	2.596	1.7	3.5	10.0
0.7 Na	"	"	.770	3.293	2.2			2.0	5.7
0.9 Li	1	0.45	.738	3.233	5.2	3.415	2.1	5.2	11.5
0.9 Na	"	"	.749	3.253	2.2			2.0	4.5
1.1 Li	1	0.55	.721	3.201	6.4	4.325	2.7	6.7	12.2
1.1 Na	"	"	.735	3.227	2.2			2.7	4.2
1.3 Li	1	0.65	.704	3.107	7.5	5.284	3.2	8.0	12.3
1.3 Na	"	"	.716	3.192	2.7			2.9	4.5
1.5 Li	1	0.75	.685	3.135	8.6	6.293	3.9	8.9	11.8
1.5 Na	"	"	.703	3.168	3.5			3.6	4.8
1.7 Li	1	0.85	.66	3.096	9.7	7.328	4.4	10.2	12.0
1.7 Na	"	"	.683	3.13	3.6			3.8	4.4
1.9 Li	1	0.95	.648	3.065	10.8	8.399	4.9	11.0	11.6
1.9 Na	"	"	.677	3.119	4.1			4.2	4.4
2.1 Li	1	1.05	.632	3.032	11.6	9.539	5.5	11.6	11.0
2.1 Na	"	"	.659	3.085	4.8			4.8	4.6

upon the same basis as that previously employed in the mixture of magnesium nitrate and strontium nitrate. The values thus obtained for the mixture of lithium bromide and sodium bromide are given in the following table.

I. LITHIUM BROMIDE ALONE.
II. " " MIXED WITH SODIUM BROMIDE.
III. SODIUM BROMIDE ALONE.
IV. " " MIXED WITH LITHIUM BROMIDE.

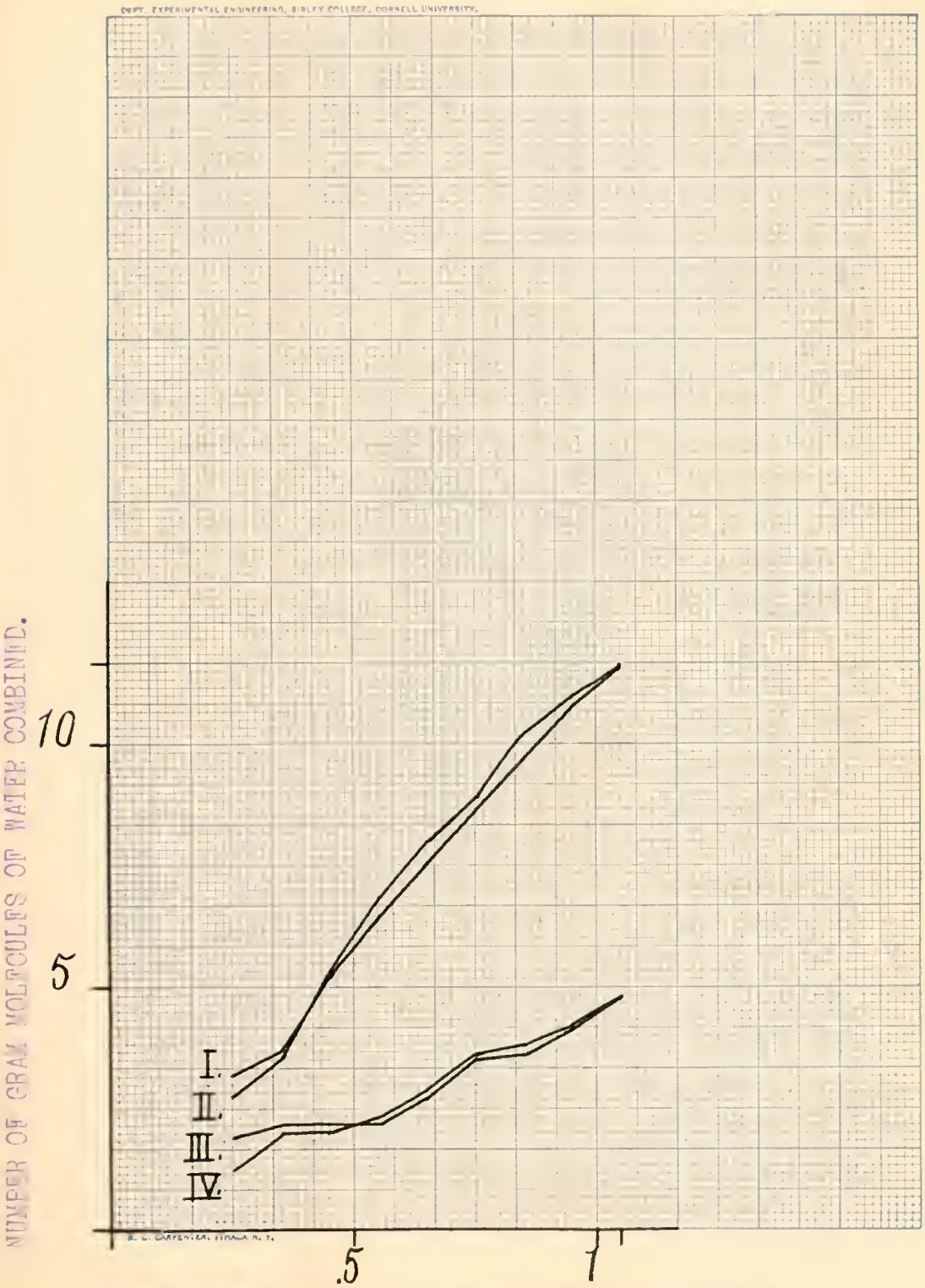

FIGURE V.

Curve II, representing the value of M in the mixture of lithium bromide and sodium bromide, crosses curve I, the value of M for lithium bromide in single solution. The same phenomenon presents itself in the case of sodium bromide, at a somewhat greater concentration. In an earlier part of this paper it was suggested that the hydrating power of the ions alone, and of these ions when combined to form molecules, would probably be different. If, now, the hydrating power of the lithium bromide and the sodium bromide molecules is greater than that of the respective ions, we might expect that the effect of the smaller amount of water present as solvent in the mixture would be overcome by the greater hydrating power of the undissociated molecules. Evidently, for this increased hydrating power of the molecules over the ions to show itself in the resulting curve, the other salt in the mixture must have little hydrating power, and a comparatively small molecular weight, for if the molecular weight is large, so much solvent will be displaced when the solutions are made up volume normal, that the decreased amount of solvent will obscure any change in hydration due to other causes. Also, the difference in the hydrating power of the ions and molecules should be considerable, in order to overcome the effect

of decrease in amount of solvent present with increase in concentration.

The difference between the amount of water acting as solvent towards each salt, in the mixture and in single solution, and the differences between the values of H in the same cases are given in the following tables. A negative value of D for H indicates that the number of grams of water eliminated by a salt in a mixture is greater, instead of less than in single solution.

Table LXXI. LITHIUM BROMIDE IN MIXTURES OF LITHIUM BROMIDE AND SODIUM BROMIDE.

M.	D_{H_2O}.	D_M.
0.35	27	0.4
0.45	45	0.2
0.45	47	0
0.55	55	-0.3
0.65	69	-0.5
0.75	85	-0.3
0.85	91	-0.5
0.95	101	-0.8
1.05	115	0

Table LXXII. SODIUM BROMIDE IN MIXTURES OF LITHIUM BROMIDE AND SODIUM BROMIDE.

L.	D_{H_2O}.	D_M.
0.25	54	0.7
0.35	72	0.2
0.45	104	0.2
0.55	144	-0.1
0.65	159	-0.2
0.75	180	- 0.1
0.85	205	-0.2
0.95	222	-0.1
1.05	276	0

These values are plotted in curves in Figures XI and XII. The fact that the curves show positive values of D_M has already been explained as probably due to the increased hydrating power of the molecule over its ions, so that when sufficient driving back in dissociation occurs we would get an increased amount of water eliminated as water of hydration. That this difference is nearly constant is to be expected, since corresponding additions of sodium bromide and lithium bromide are always made, in changes of concentration.

DIFFERENCE BETWEEN THE AMOUNT OF WATER PRESENT AS SOLVENT IN THE SINGLE SOLUTION OF LITHIUM BROMIDE AND IN THE MIXTURE OF LITHIUM BROMIDE AND SODIUM BROMIDE DIFFERENCE BETWEEN THE VALUES OF M FOR LITHIUM BROMIDE IN SINGLE SOLUTION AND IN THE MIXTURE OF LITHIUM BROMIDE AND SODIUM BROMIDE.

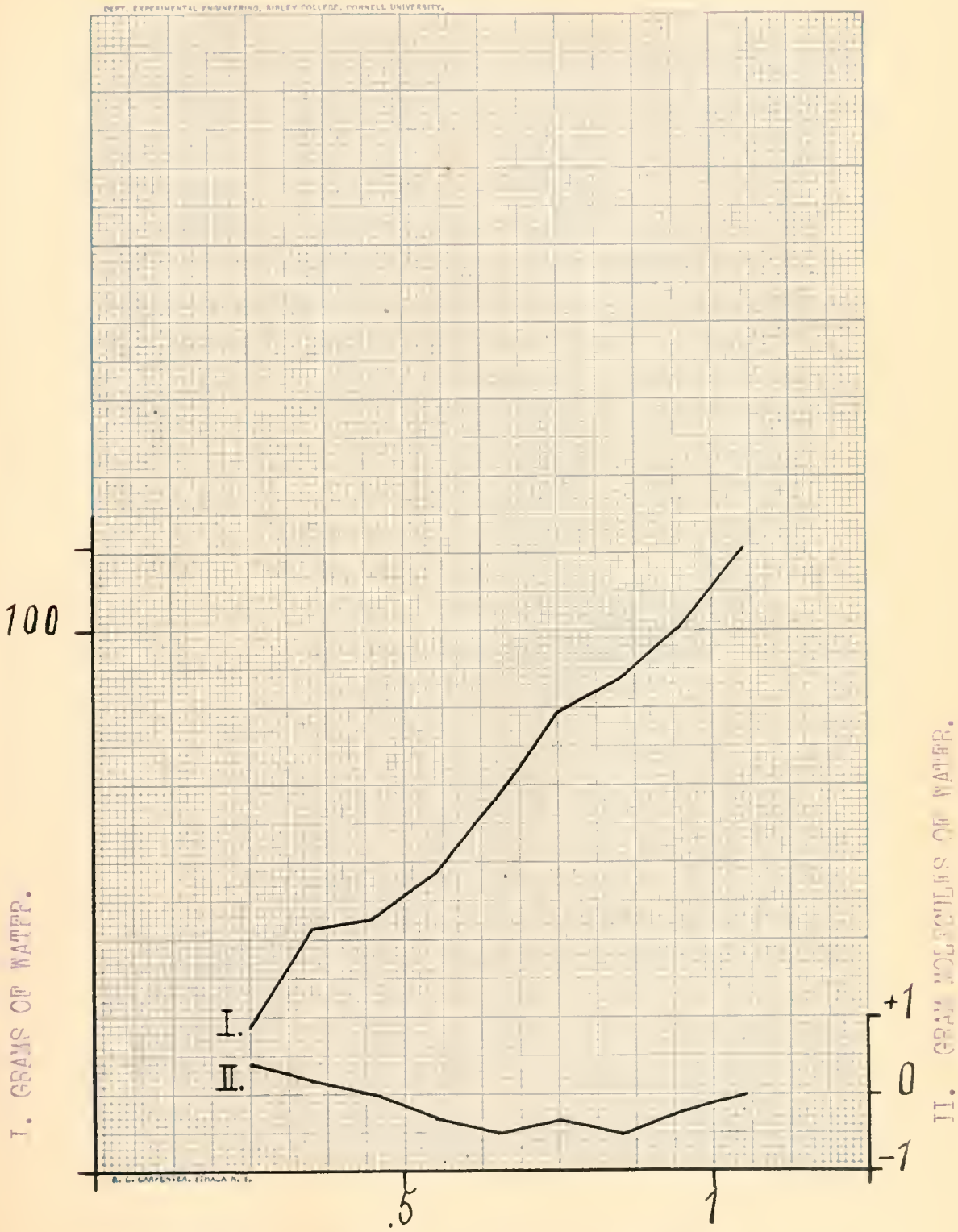

FIGURE VI.

DIFFERENCE BETWEEN THE AMOUNT OF WATER PRESENT AS SOLVENT IN THE SINGLE SOLUTION OF SODIUM BROMIDE AND IN THE MIXTURE OF SODIUM BROMIDE AND LITHIUM BROMIDE

DIFFERENCE BETWEEN THE VALUES OF X FOR SODIUM BROMIDE IN SINGLE SOLUTION AND IN THE MIXTURE OF SODIUM BROMIDE AND LITHIUM BROMIDE.

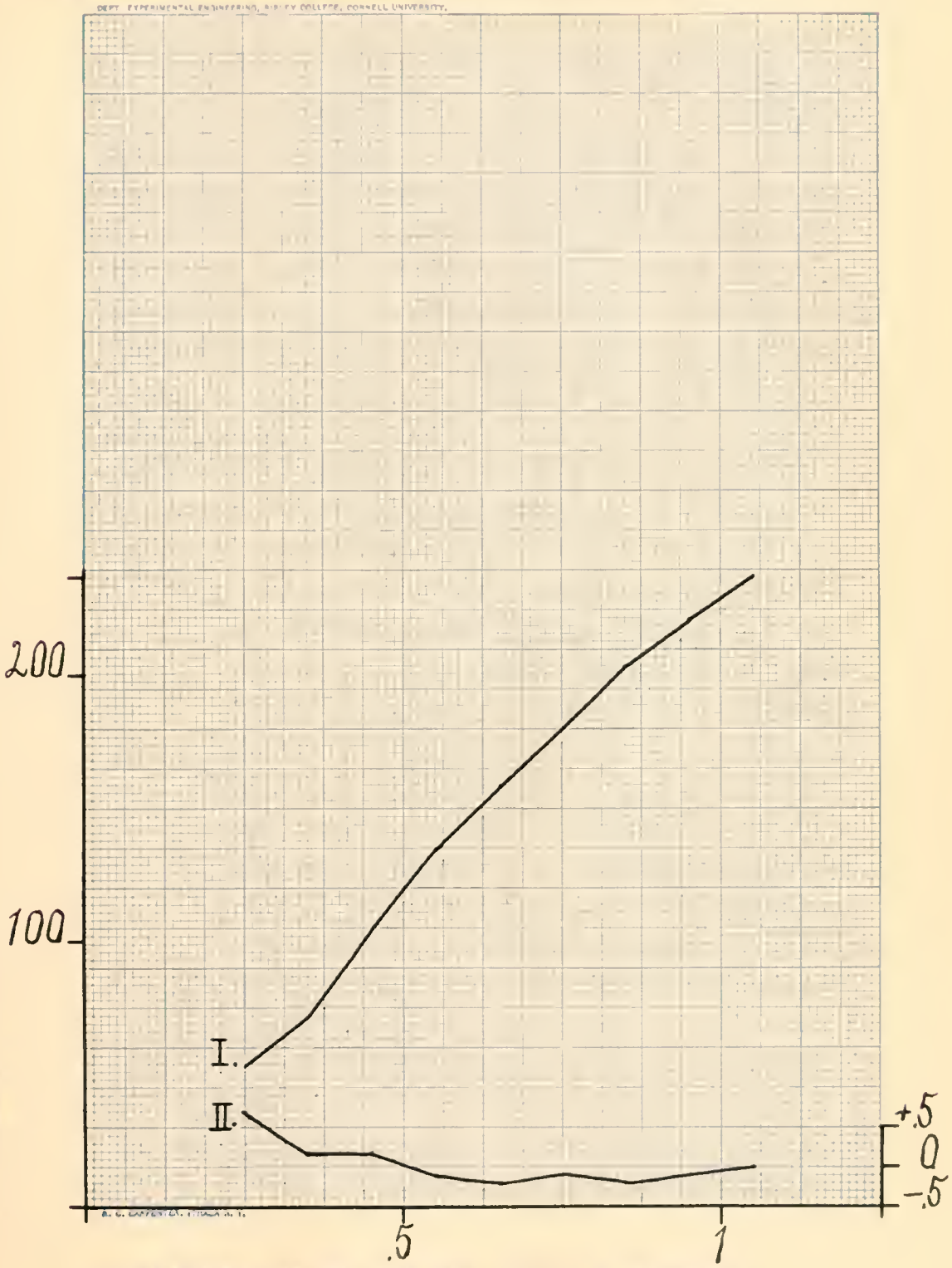

FIGURE XII.

We next consider a Mixture of Calcium Nitrate and Magnesium Nitrate, Both of which Have Hydrating Power.

CALCIUM NITRATE.

Table LXXIII. FREEZING-POINT MEASUREMENTS.

m.	Δ.	Δ/m.
0.25	1°189	4.756
0.45	2.094	4.65
0.65	3.041	4.68
0.85	4.057	4.77
1.05	5.123	4.88
1.25	6.345	5.08
1.45	7.547	5.21
1.6555	8.859	5.35

Table LXXIV. CONDUCTIVITY MEASUREMENTS.

m.	v.	k.	Λ_v.	α.
0.25	4.0000	.020975	83.9	0.624
0.45	2.2222	.033259	73.9	.550
0.65	1.538	.042932	66.0	.491
0.85	1.1765	.050272	59.2	.440
1.05	0.9525	.056301	53.6	.399
1.25	0.8000	.060363	48.3	.359
1.45	0.6897	.063236	43.6	.324
1.6555	0.6041	.064674	39.1	.291

Table LXXV. WEIGHT-NORMAL CORRECTIONS.

m.	$W_{Sol.}$	$W_{Salt.}$	W_{H_2O}.	Correction Per Cent.
0.25	25.77665	1.026	24.7405	1.0
0.45	26.3748	1.8467	24.5281	1.9
0.65	26.9697	2.6674	24.3019	2.8
0.85	27.5168	3.4883	24.286	3.9
1.05	28.1060	4.3089	23.7971	4.8
1.25	28.6822	5.1297	23.5525	5.8
1.45	29.2340	5.9504	23.2836	6.9
1.6555	29.8480	6.7938	23.0542	7.8

Table LXXVI. HYDRATES.

m.	α.	L.	Δ/m.	L'.	M.	H.
0.25	0.624	4.18	4.76	4.71	6.3	25.2
0.45	.550	3.90	4.65	4.56	8.0	17.9
0.65	.491	3.69	4.68	4.55	10.5	16.2
0.85	.440	3.50	4.77	4.58	13.1	15.4
1.05	.391	3.34	4.88	4.65	15.7	15.0
1.25	.359	3.20	5.08	4.79	18.4	14.7
1.45	.324	3.07	5.21	4.85	20.4	14.1
1.6555	.291	2.94	5.35	4.93	22.4	13.5

MAGNESIUM NITRATE.

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Table LXXVII. FREEZING-POINT MEASUREMENTS.

m.	Δ.	Δ/m.
0.25	1°252	5.01
0.45	2.495	5.52
0.65	3.669	5.64
0.85	5.113	6.02
1.05	6.762	6.44
1.25	8.562	6.85
1.45	10.589	7.30

Table LXXVIII. CONDUCTIVITY MEASUREMENTS.

Λ_∞, 0°, = 128.5.

m.	v.	k.	Λ_v.	α 0.671.
0.25	4.0000	.031563	86.3	
0.45	2.2222	.035123	78.1	.607
0.65	1.538	.046942	72.2	.562
0.85	1.1765	.056821	66.9	.520
1.05	0.9525	.065354	62.2	.484
1.25	0.8000	.071668	57.7	.446
1.45	0.68966	.076279	52.6	.409

Table LXXIX. WEIGHT-NORMAL CORRECTIONS.

m.	$W_{Sol.}$	$W_{Salt.}$	W_{H_2O}.	Correction Per Cent.
0.25	25.6[illegible]8	0.9277	24.7605	1.0
0.45	26.2075	1.6699	24.5376	1.8
0.65	26.7605	2.4122	24.3483	2.6
0.85	27.1958	3.1543	24.0415	3.8
1.05	27.7080	3.8965	23.8115	4.8
1.25	28.2485	4.6287	23.6048	5.6
1.45	28.7626	5.3809	23.3817	6.5

Table LXXX. HYDRATES.

m.	α .	L.	Δ/m.	L'.	M.	H.
0.25	0.671	4.86	5.01	4.96	6.7	26.8
0.45	.607	4.12	5.32	5.22	11.7	26.0
0.65	.562	3.95	5.64	5.49	15.6	24.0
0.85	.520	3.80	6.02	5.79	19.1	22.5
1.05	.484	3.66	6.44	6.13	22.4	21.3
1.25	.446	3.52	6.85	6.47	25.3	20.2
1.45	.409	3.38	7.30	6.83	28.1	19.4

Data for the Mixture of CALCIUM NITRATE and MAGNESIUM NITRATE follows.

Table LXXXI. FREEZING-POINT MEASUREMENTS.

m.	P.	Δ.
0.5 $Ca(NO_3)_2$ 0.5 $Mg(NO_3)_2$	1 "	2°498
0.9 $Ca(NO_3)_2$ 0.9 $Mg(NO_3)_2$	1 "	4.856
1.3 $Ca(NO_3)_2$ 1.3 $Mg(NO_3)_2$	1 "	7.684
1.7 $Ca(NO_3)_2$ 1.7 $Mg(NO_3)_2$	1 "	10.93
2.1 $Ca(NO_3)_2$ 2.1 $Mg(NO_3)_2$	1 "	19.90
2.5 $Ca(NO_3)_2$ 2.5 $Mg(NO_3)_2$	1 "	19.73
2.9 $Ca(NO_3)_2$ 2.9 $Mg(NO_3)_2$	1 "	24.8

Table LXXXII. WEIGHT-NORMAL CORRECTIONS.

m.	P.	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction Per Cent.
0.5 $Ca(NO_3)_2$ 0.5 $Mg(NO_3)_2$	1 "	26.4387	1.9537	24.4850	2.1
0.9 $Ca(NO_3)_2$ 0.9 $Mg(NO_3)_2$	1 "	27.5700	3.5166	24.0131	3.9
1.3 $Ca(NO_3)_2$ 1.3 $Mg(NO_3)_2$	1 "	28.5974	5.0796	23.5178	5.9
1.7 $Ca(NO_3)_2$ 1.7 $Mg(NO_3)_2$	1 "	29.6600	6.6425	23.0175	7.9
2.1 $Ca(NO_3)_2$ 2.1 $Mg(NO_3)_2$	1 "	30.6253	8.2055	22.4198	10.3
2.5 $Ca(NO_3)_2$ 2.5 $Mg(NO_3)_2$	1 "	31.6538	9.7684	21.8854	12.5
2.9 $Ca(NO_3)_2$ 2.9 $Mg(NO_3)_2$	1 "	32.9175	11.6313	21.2862	14.9

Table LXXXIII. CONDUCTIVITY MEASUREMENTS.

m.	P.	m_c.	v_c.	k_w.	R.	D.	k_c.	Λ_v	α.
0.5 Ca_2NO_3	1	0.85	4.0000	.036833	.020975	.003705	.019014	76.1	0.
0.5 Mg_2NO_3	"	"	"		.021[illegible]		.019820	79.7	.71
0.9 Ca	1	0.45	2.2222	.054700	.033259	.017682	.025920	57.6	.428
0.9 Mg	"	"	"		.035123		.028720	64.0	.498
1.3 Ca	1	0.65	1.538	.065970	.042932	.028904	.029904	46.0	.342
1.3 Mg	"	"	"		.046942		.036066	55.5	.432
1.7 Ca	1	0.85	1.1765	.071201	.050272	.035892	.030420	35.8	.266
1.7 Mg	"	"	"		.056831		.040781	8.	.73
2.1 Ca	1	1.05	0.9523	.071673	.056301	.04[illegible]2	.028832	27.[illegible]	.201
2.1 Mg	"	"	"		.065774		.043741	41.8	.
2.5 Ca	1	1.25	0.8000	.069140	.060763	.002891	.024807	19.9	8
2.5 Mg	"	"	"		.071068		.044[illegible]	35.5	.276
2.9 Ca	1	1.45	0.6896	.063327	.063836	.076188	.019866	13.7	.102
2.9 Mg	"	"	"		.070279		.043461	30.0	2[illegible]3

Table LXXXIV. HYDRATES.

m.	P.	m_c.	α.	L_c.	M.	Δ.	Sp.Gr. Cor.	M_c.	N_c.
0.5 $Ca(NO_3)_2$	1	0.25	0.565	3.96	6.3	2°498	2.1	4.6	18.5
0.5 $Mg(NO_3)_2$	"	"	.617	4.16	6.7			5.8	20.8
0.9 Ca	1	0.45	.428	3.45	8.0	4.856	3.9	7.8	16.0
0.9 Mg	"	"	.498	3.71	11.7			11.1	24.7
1.3 Ca	1	0.65	.342	3.13	10.5	7.624	5.9	9.4	14.4
1.3 Mg	"	"	.432	3.47	15.6			14.9	22.9
1.7 Ca	1	0.85	.266	2.85	13.1	10.93	7.9	11.7	13.8
1.7 Mg	"	"	.373	3.25	19.1			18.1	21.3
2.1 Ca	1	1.05	.201	2.61	15.7	14.90	10.3	15.6	13.0
2.1 Mg	"	"	.321	3.05	22.4			21.0	20.0
2.5 Ca	1	1.25	.148	2.41	18.4	19.73	12.5	15.7	12.5
2.5 Mg	"	"	.276	2.89	25.3			25.3	18.7
2.9 Ca	1	1.45	.102	2.24	20.4	24.8	14.9	16.5	11.4
2.9 Mg	"	"	.233	2.73	28.1			25.2	17.4

The values of M for each salt in the mixture and in separate solution are plotted in curves in Figure XIII. With increased concentration we have increased divergence in curves I and III which represent the hydrating power(values of M) in separate solutions of magnesium nitrate and of calcium nitrate, respectively. Consequently, as we should expect, curves II and IV, representing the values of M of the two salts in the mixture, show increasing divergence with increase in concentration.

MAGNESIUM NITRATE ALONE.
" " MIXED WITH CALCIUM NITRATE.
CALCIUM NITRATE ALONE.
" " MIXED WITH MAGNESIUM NITRATE.

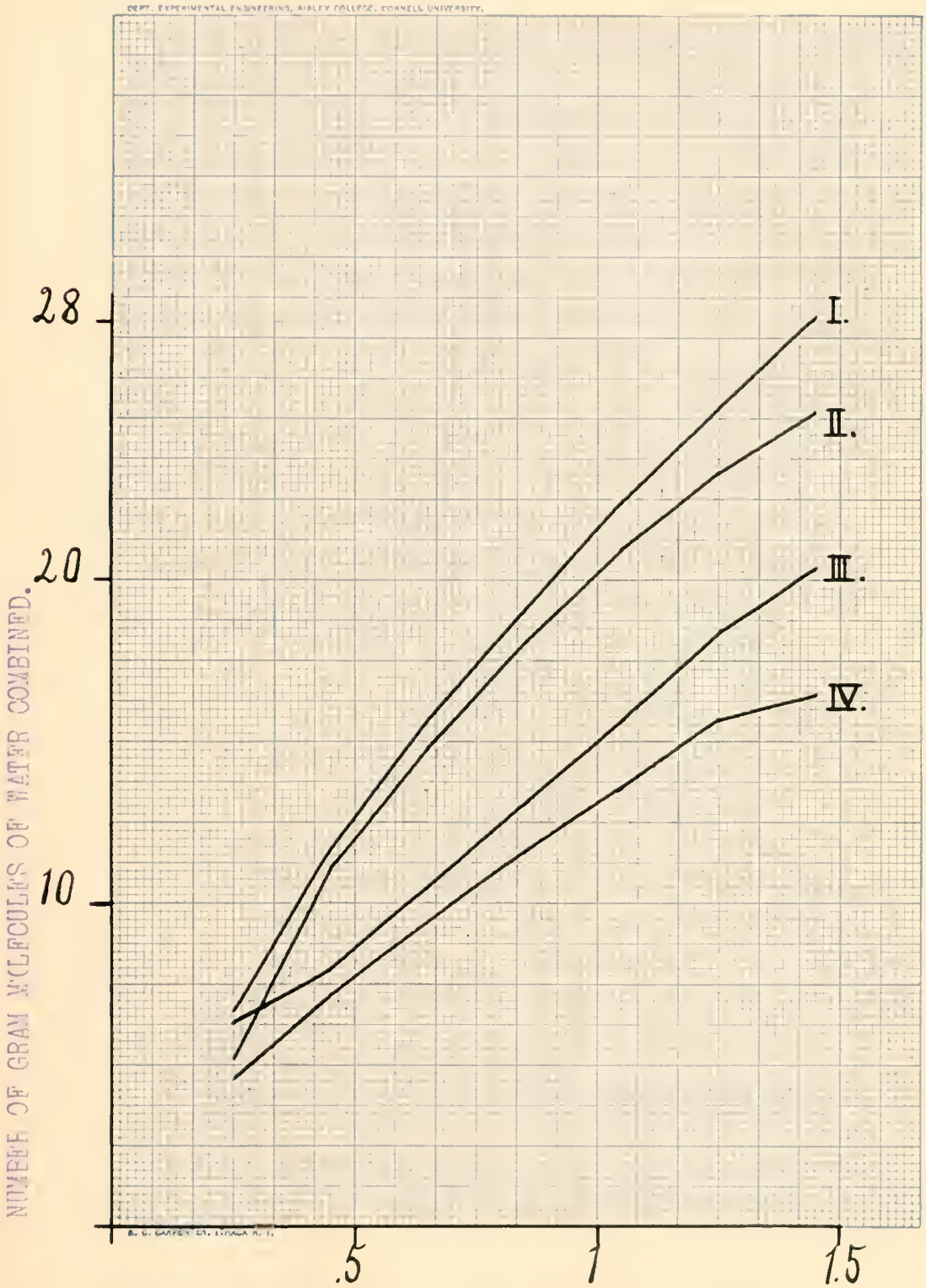

FIGURE XIII.

Table LXXXVI. CALCIUM NITRATE IN MIXTURE OF CALCIUM NITRATE AND MAGNESIUM NITRATE.

m.	D_{H_2O}.	D_M.
0.25	104.4	1.7
0.45	220.3	0.8
0.65	298.5	1.1
0.85	365.7	1.4
1.05	432.5	2.1
1.25	487	2.7
1.45	534	3.9

Table LXXXVII MAGNESIUM NITRATE IN MIXTURE OF CALCIUM NITRATE AND MAGNESIUM NITRATE.

m.	D_{H_2O}.	D_M.
0.25	93.7	1.5
0.45	150.5	0.6
0.65	202	0.7
0.85	251	1.0
1.05	300	1.4
1.25	351	2.0
1.45	381	2.9

These values are plotted in curves in Figures XIV and XV.

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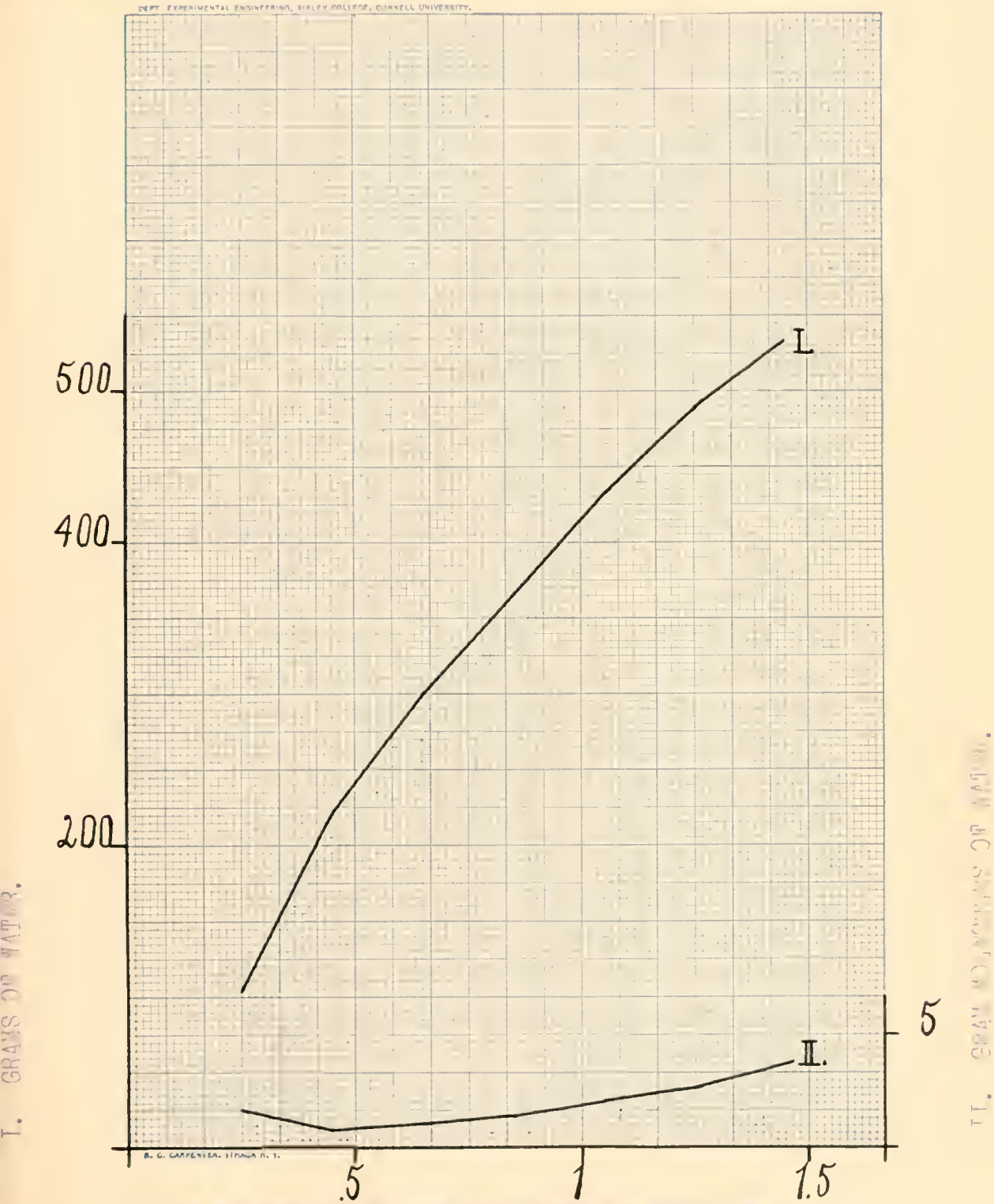
DIFFERENCE BETWEEN THE AMOUNT OF WATER PRESENT AS SOLVENT IN THE SINGLE SOLUTION OF CALCIUM NITRATE AND IN THE MIXTURE OF CALCIUM NITRATE AND MAGNESIUM NITRATE.

DIFFERENCE BETWEEN THE VALUES OF 1 FOR CALCIUM NITRATE IN SINGLE SOLUTION AND IN THE MIXTURE OF CALCIUM NITRATE AND MAGNESIUM NITRATE.

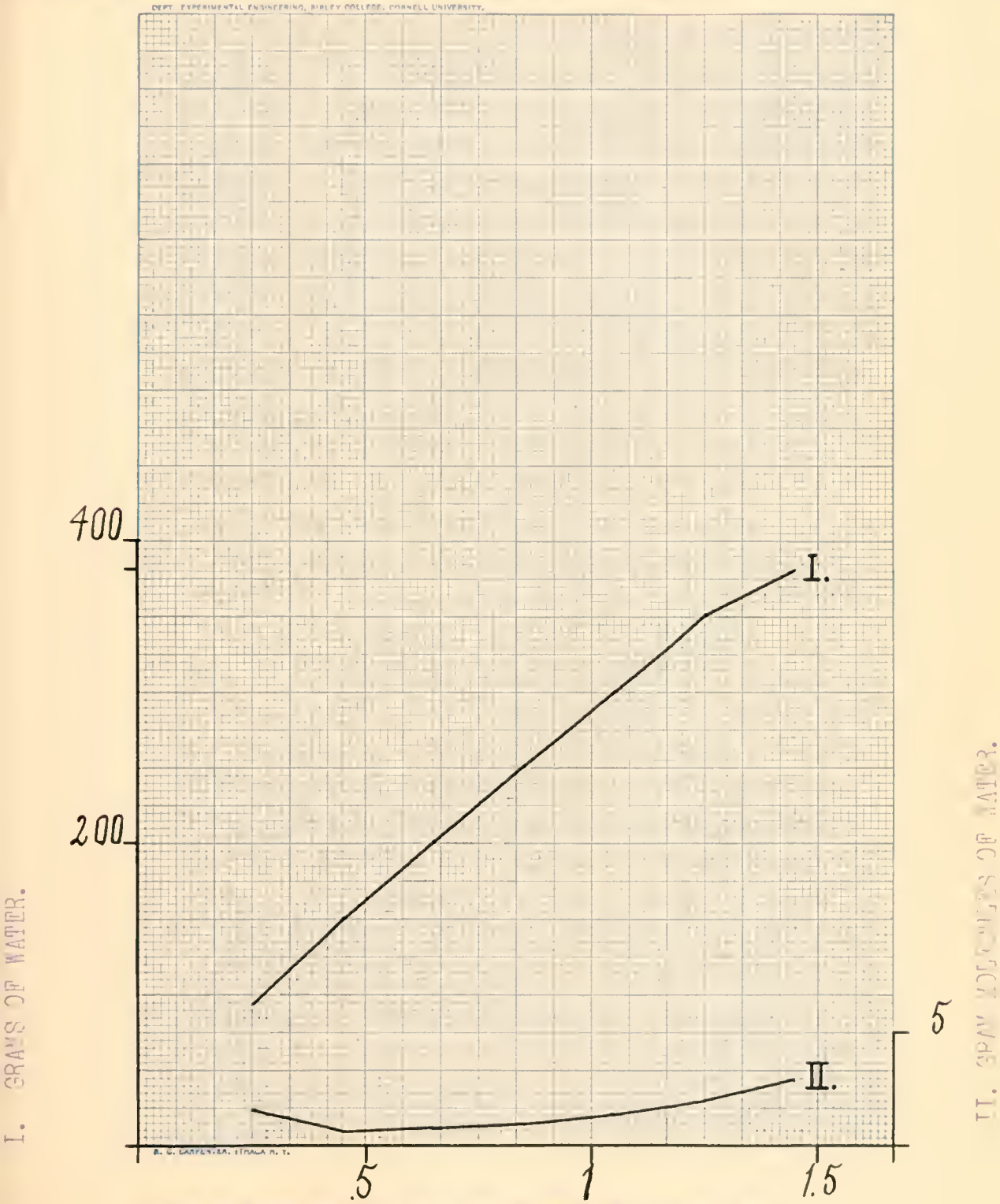


GRAM MOLECULES OF SALT PER LITER OF SOLUTION.

FIGURE XIV.

DIFFERENCE BETWEEN THE AMOUNT OF WATER PRESENT AS SOLVENT IN THE CANCER SOLUTION OF MAGNESIUM NITRATE AND IN THE MIXTURE OF MAGNESIUM NITRATE AND CALCIUM NITRATE.

DIFFERENCE BETWEEN THE VALUES OF M FOR MAGNESIUM NITRATE IN FINALE SOLUTION AND IN THE MIXTURE OF CALCIUM NITRATE AND MAGNESIUM NITRATE.



GRAM MOLECULES OF SALT PER LITER OF SOLUTION.

FIGURE XV.

The curves in Figures XIV and XV show the same general relations as the preceding curves of the same character, excepting those of lithium bromide and sodium bromide. The amount of water eliminated to form hydrates in the mixture, tends to diminish somewhat proportionally to the diminution in the amount of water present which is acting as solvent. This is clearly shown by the direction in which the curves turn with increased concentration of the solutions. It is probable that in the more dilute solutions we have the difference in the hydrating power of the ions and molecules affecting the total amount of water eliminated as water of hydration. Consequently, where the total amount of salt is constant, but a change in the dissociation is produced, if the number of ions is large relative to the number of molecules undissociated, as is the case in the more dilute solutions, the curve for D_M does not at once show the influence of diminishing amount of solvent present. This phenomenon is shown by the curves as change of direction, or increased curvature in the curve which represents the value of D_M.

A Pair of Quaternary Electrolytes was Next Studied. Ferric chloride and aluminium chloride were employed. Very concentrated stock solutions were prepared, and the necess-

ary measurements were made as quickly as possible, in orde to reduce hydrolysis to a minimum, there being a time facto in the hydrolysis of such compounds as ferric chlo . Notwithstanding all precautions there was, of course, considerable hydrolysis. Especially was this the case in the mixture of the two salts, the presence of the aluminium chloride appearing to act catalytically upon the solution of ferric chloride, causing a gradual precipitation of hydroxide of iron.

ALUMINIUM CHLORIDE.

Table LXXXVIII. FREEZING-POINT MEASUREMENTS.

m.	Δ.	Δ/m.
0.2	1°279	6.40
0.4	2.910	7.28
0.6	5.144	8.57
0.8	7.962	9.95
1.0	11.795	11.80
1.2	16.385	13.65
1.3617	21.75	15.97
1.415	23.5	16.6

Table LXXXIX. CONDUCTIVITY MEASUREMENTS.

m.	v.	k.	Λ_v.	α.
0.2	5.000	.023983	119.9	0.660
0.4	2.500	.04053	101.3	.558
0.6	1.6666	.058115	88.5	.487
0.8	1.250	.06118	76.5	.421
1.0	1.000	.066595	66.6	.367
1.2	0.8333	.06842	57.0	.314
1.3617	0.7344	.06760	49.7	.273

Table XC. WEIGHT-NORMAL CORRECTIONS.

m.	$W_{Sol.}$	$W_{Salt.}$	W_{H_2O}.	Correction Per Cent.
0.2	25.6340	0.6673	24.9567	0.2
0.4	26.1538	1.3346	24.8192	0.7
0.6	26.7134	2.0019	24.7115	1.2
0.8	27.2153	2.6693	24.5461	1.8
1.0	27.7351	3.3365	24.3986	2.4
1.2	28.2977	4.0038	24.2839	2.9
1.3617	28.7252	4.5433	24.1819	3.3

Table XCI. HYDRATES.

m.	α.	L.	Δ/m.	L'.	M.	H.
0.2	0.660	5.54	6.40	6.39	7.4	37.0
0.4	.558	4.97	7.28	7.23	17.4	43.5
0.6	.487	4.58	8.57	8.47	25.5	42.5
0.8	.421	4.21	9.95	9.77	31.6	39.5
1.0	.367	3.91	11.80	11.52	36.7	36.7
1.2	.314	3.61	13.65	13.25	40.4	33.7
1.3617	.273	3.39	15.97	15.44	43.4	31.9

FERRIC CHLORIDE.

Table XCII. FREEZING-POINT MEASUREMENTS.

m.	Δ.	Δ/m.
0.2	1°255	6.28
0.4	2.715	6.79
0.6	4.530	7.55
0.8	6.667	8.33
1.0	9.152	9.15
1.2	12.11	10.09
1.3617	14.592	10.72

Table XCIII. CONDUCTIVITY MEASUREMENTS.

$\Lambda_{\infty}, 0° = 220.$ (Calculated).

m.	v.	k.	Λ_v.	α.
0.2	5.000	.02380	119.0	0.541
0.4	2.500	.03786	94.7	.430
0.6	1.6666	.04645	77.4	.352
0.8	1.250	.05147	64.3	.292
1.0	1.000	.053147	53.1	.241
1.2	0.8333	.053145	44.3	.201
1.3617	0.7344	.051777	38.0	.173

Table XCIV. WEIGHT-NORMAL CORRECTIONS.

m.	$W_{Sol.}$	$W_{Salt.}$	W_{H_2O}.	Correction Per Cent.
0.2	25.6792	0.8113	24.8679	0.5
0.4	26.3380	1.6225	24.7155	1.1
0.6	26.9956	2.4337	24.5619	1.8
0.8	27.6250	3.245	24.378	2.5
1.0	28.2400	4.056	24.184	3.3
1.2	28.8667	4.8675	24.0192	3.9
1.3617	29.3690	5.5334	23.8456	4.6

Table XCV. HYDRATES.

m.	α.	L.	Δ/m.	L'.	M.	H.
0.2	0.541	4.88	6.28	6.25	12.2	61.0
0.4	.430	4.26	6.79	6.72	20.3	50.7
0.6	.352	7.32	7.55	7.41	26.9	44.8
0.8	.292	7.49	8.33	8.12	31.7	39.6
1.0	.241	8.21	9.15	8.85	35.4	35.4
1.2	.201	8.98	10.09	9.70	38.5	32.1
1.3617	.173	2.82	10.22	10.23	40.2	29.5

MIXTURE OF FERRIC CHLORIDE AND ALUMINIUM CHLORIDE.

Table XCVI. FREEZING-POINT MEASUREMENTS.

m.	P.	Δ.
0.4 $FeCl_3$ 0.4 $AlCl_3$	1 "	2°938
0.8 $FeCl_3$ 0.8 $AlCl_3$	1 "	7.288
1.2 $FeCl_3$ 1.2 $AlCl_3$	1 "	13.69
1.6 $FeCl_3$ 1.6 $AlCl_3$	1 "	22.5
2.0 $FeCl_3$ 2.0 $AlCl_3$	1 "	36.0
2.4 $FeCl_3$ 2.4 $AlCl_3$	1 "	56.0
2.7234 $FeCl_3$ 2.7234 $AlCl_3$	1 "	84.6

It was necessary to extrapolate this last value, 84°6, since the solution failed to freeze in the freezing mixture

employed, i,e,solid carbon dioxide and alcohol. The more concentrated solutions became so viscous, when cooled down, that it was difficult to stir them properly.

Table XCVII. WEIGHT-NORMAL CORRECTIONS.

m.	P.	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction Per Cent.
0.4 $FeCl_3$ 0.4 $AlCl_3$	1 "	26.2807	1.4786	24.8021	0.8
0.8 $FeCl_3$ 0.8 $AlCl_3$	1 "	27.4365	2.9571	24.4794	2.1
1.2 $FeCl_3$ 1.2 $AlCl_3$	1 "	28.5660	4.4356	24.1304	3.5
1.6 $FeCl_3$ 1.6 $AlCl_3$	1 "	29.7105	5.9142	23.7963	4.8
2.0 $FeCl_3$ 2.0 $AlCl_3$	1 "	30.8182	7.3925	23.4257	6.3
2.4 $FeCl_3$ 2.4 $AlCl_3$	1 "	31.9182	8.8713	23.0469	7.8
2.7234 $FeCl_3$ 2.7234 $AlCl_3$	1 "	32.7777	10.0667	22.7110	9.2

It is to be noted that the conductivity measurements, which are given in the following table, are the nearest approximations, as measurements of dissociation. The conductivity measurements were made at zero, whereas some of these mixtures freeze very considerably below 0°,C. There is marked hydrolysis, in some cases, as already mentioned, leading to a precipitation of the iron. There is considerable difference between the viscosity of the single solutions

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and of the mixtures where the normalities are the same. The assumption that these salts dissociate at once, in the most concentrated solutions, into $\overset{+}{K}, \overset{-}{Cl}, \overset{-}{Cl}, \overset{-}{Cl}$, is certainly not correct. Finally, the values of Λ_{∞} are calculated values and may differ conciderably from the true values, because of the factors just mentioned.

Table XCVIII. CONDUCTIVITY MEASUREMENTS.

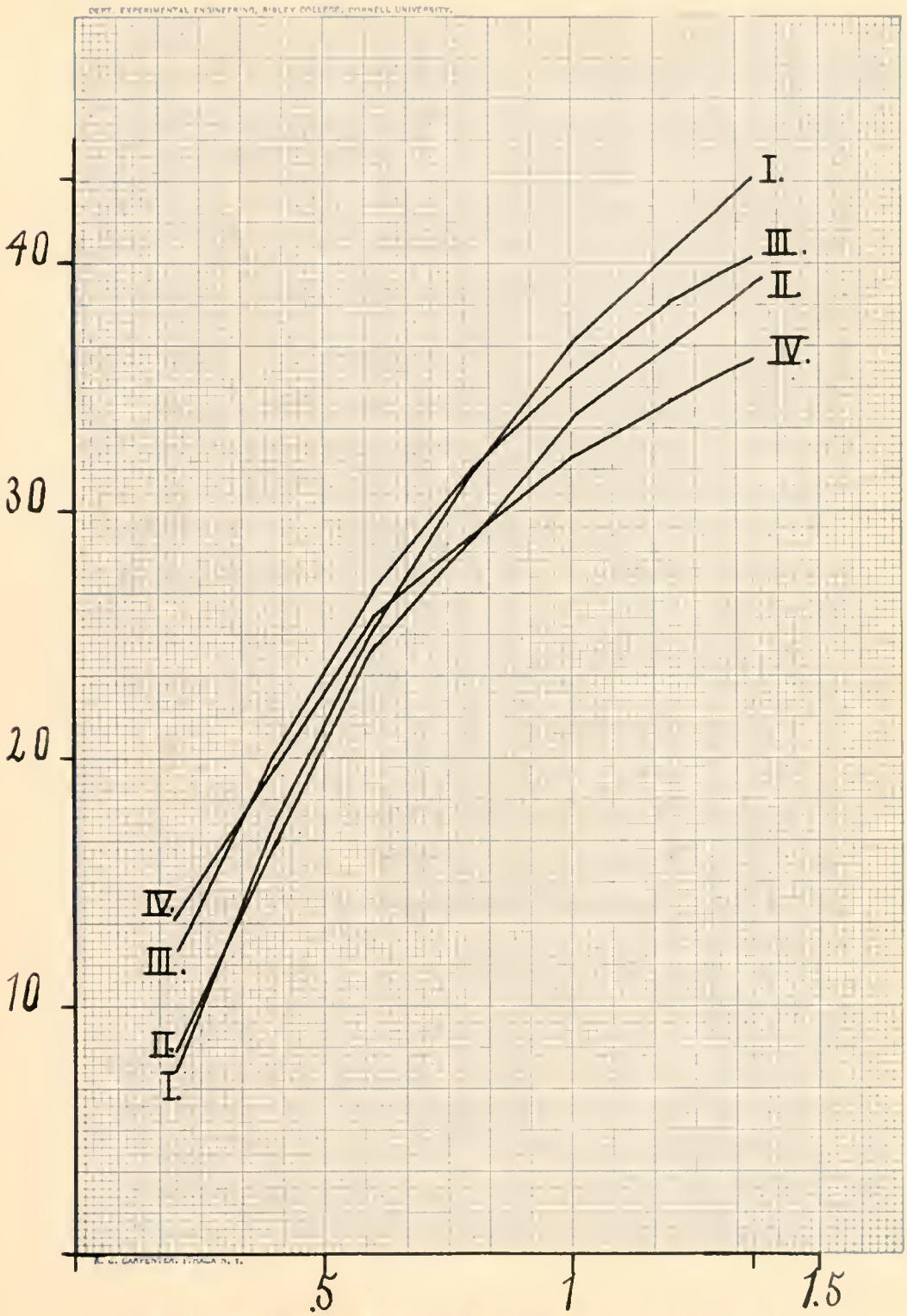
m.	P.	m_c.	v_c.	k_w.	k.	D.	k_c.	Λ_v	a.
0.4 $FeCl_3$	1	0.2	5.000	.040818	.02780	.007465	.01985	97.8	0.140
0.4 $AlCl_3$	"	"	"		.027983		.020968	104.8	.577
0.8 Fe	1	0.4	2.500	.060462	.03786	.017928	.026928	67.3	.306
0.8 Al	"	"	"		.04053		.033534	83.7	.461
1.2 Fe	1	0.6	1.6666	.058874	.04645	.043691	.019059	31.8	.144
1.2 Al	"	"	"		.058115		.036815	61.4	.338
1.6 Fe	1	0.8	1.250	.056904	.05147	.0[illegible]575	.01604	20.1	.091
1.6 Al	"	"	"		.06118		.04086	51.1	.321
2.0 Fe	1	1.0	1.00	.047916	.053147	.071836	.006597	6.6	.030
2.0 Al	"	"	"		.066595		.041819	41.3	.227
2.4 Fe	1	1.2	0.8333	.037866	.053145	.083699	.00000	00.0	.00
2.4 Al	"	"	"		.06842		.03787	31.6	.174
2.7834 Fe	1	1.36170.7344		.029595	.051777	.089782	.0000	00.0	.00
" Al	"	"	"		.06760		.029595	21.7	.120

Table XCIX. HYDRATES.

m.	P.	m_c.	α.	L_c.	M.	Δ.	SpGr. Cor.	M_c.	H_c.
0.4 $FeCl_3$	1	0.2	0.440	4.31	12.2	2°978	0.8	13.5	37.5
0.4 $AlCl_3$	"	"	.577	5.08	7.4			8.2	41.0
0.8 Fe	1	0.4	.306	3.57	20.3	7.288	2.1	19.6	49.0
0.8 Al	"	"	.461	4.44	17.4			16.6	41.5
1.2 Fe	1	0.6	.144	2.67	26.9	13.69	3.5	25.8	47.0
1.2 Al	"	"	.338	3.74	25.5			24.4	40.7
1.6 Fe	1	0.8	.091	2.37	31.7	22.5	4.8	29.0	36.2
1.6 Al	"	"	.281	3.43	31.6			28.9	36.1
2.0 Fe	1	1.0	.050	2.03	35.4	36.0	6.3	32.2	32.2
2.0 Al	"	"	.227	3.02	36.7			35.7	33.7
2.4 Fe	1	1.2	.00	1.86	38.5	56.0	7.8	34.6	28.8
2.4 Al	"	"	.174	2.83	40.4			36.7	30.6
2.7284 Fe	1	1.3617	.00	1.86	40.2	84.6	9.2	36.1	26.5
" Al	"	"	.120	2.53	43.4			39.6	29.0

These values of M and of M_c are plotted in curves in Figure XVI. The general relations shown by these curves are the same as have previously been pointed out. The fact that the hydrating power of both the aluminium chloride and the ferric chloride is apparently greater in the mixture than in the separate solutions, in the most dilute solutions employed, is probably due to the effect of hydrolysis in increasing the value of L, and consequently diminishing M, though possibly partially due to change in dissociation and difference in the hydrating power of the ions and molecules. It should be noted, also, that the hydrating power of the aluminium chloride appears to be relatively less than that of the ferric chloride in the more dilute solutions; but that this relation is reversed in the more concentrated solutions. This may be due to hydrolysis, since if the aluminium chloride hydrolyzes more rapidly than the ferric chloride, then, in the more dilute solutions, where the effects of hydrolysis would be pronounced, the result would be to increase the value of L and, consequently, to diminish the value of M, based upon it.

ALUMINUM CHLORIDE ALONE.
" " MIXED WITH FERRIC CHLORIDE.
I. FERRIC CHLORIDE ALONE.
" " MIXED WITH ALUMINUM CHLORIDE.



GRAM MOLECULES OF SALT PER LITER OF SOLUTION.

FIGURE XVI.

In Tables C and CI the abbreviations have the usual significance.

Table C. ALUMINIUM CHLORIDE IN MIXTURE OF ALUMINIUM CHLORIDE AND FERRIC CHLORIDE.

m.	D_{H_2O}.	D_M.
0.2	249	-0.8
0.4	367	0.8
0.6	488	1.1
0.8	552	2.7
1.0	618	3.0
1.2	671	3.7
1.3617	709	3.8

Table CI. FERRIC CHLORIDE IN MIXTURE OF ALUMINIUM CHLORIDE AND FERRIC CHLORIDE.

m.	D_{H_2O}.	D_M.
0.2	150	-1.3
0.4	308	0.7
0.6	456	1.1
0.8	543	2.7
1.0	636	3.2
1.2	699	3.9
1.3617	758	4.1

These values are plotted in curves in Figures XVII and XVIII.

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[illegible]

[illegible]

[illegible]	[illegible]	[illegible]
0.0	[illegible]	-0.0
0.1	[illegible]	0.8
0.0	[illegible]	1.1
0.0	[illegible]	0.7
1.0	[illegible]	0.0
1.0	[illegible]	0.1
1.0[illegible]	[illegible]	0.8

[illegible]

[illegible]	[illegible]	[illegible]
0.0	[illegible]	-1.7
0.4	[illegible]	0.7
0.0	[illegible]	1.1
0.0	[illegible]	0.7
1.0	[illegible]	0.0
1.0	[illegible]	0.0
1.0[illegible]	[illegible]	1.1

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DIFFERENCE BETWEEN THE AMOUNT OF WATER PRESENT AS SOLVENT IN THE SINGLE SOLUTION OF ALUMINIUM CHLORIDE AND IN THE MIXTURE OF FERRIC CHLORIDE AND ALUMINIUM CHLORIDE. DIFFERENCE BETWEEN THE VALUES OF M FOR ALUMINIUM CHLORIDE IN SINGLE SOLUTION AND IN THE MIXTURE OF ALUMINIUM CHLORIDE AND FERRIC CHLORIDE.

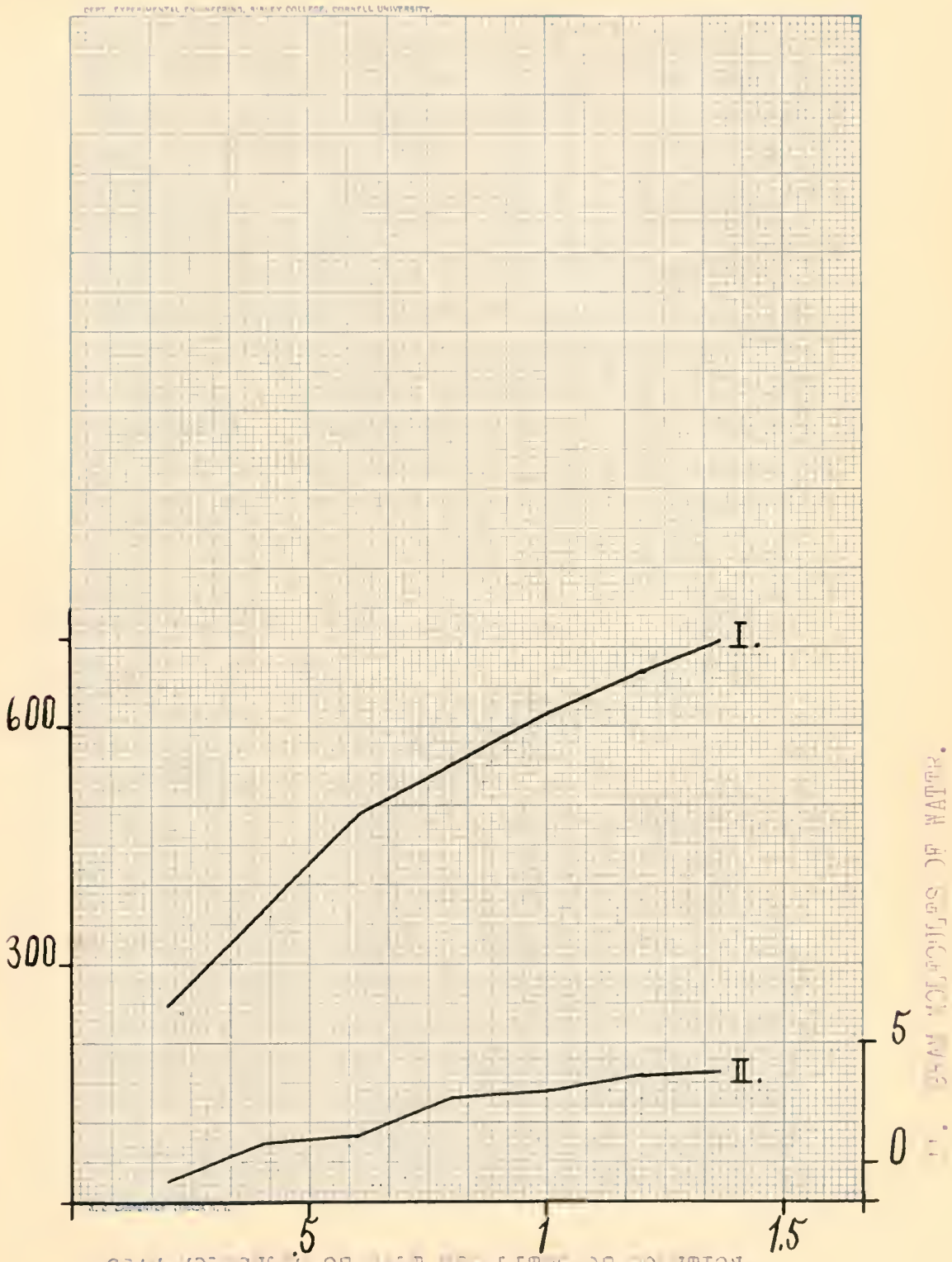

FIGURE XVII.

DIFFERENCE BETWEEN THE AMOUNT OF FERRIC PRESENT AS SOLVENT IN THE SINGLE SOLUTION OF FERRIC CHLORIDE AND IN THE MIXTURE OF FERRIC CHLORIDE AND ALUMINIUM CHLORIDE.

DIFFERENCE BETWEEN THE VALUES OF M FOR FERRIC CHLORIDE IN SINGLE SOLUTION AND IN THE MIXTURE OF FERRIC CHLORIDE AND ALUMINIUM CHLORIDE.

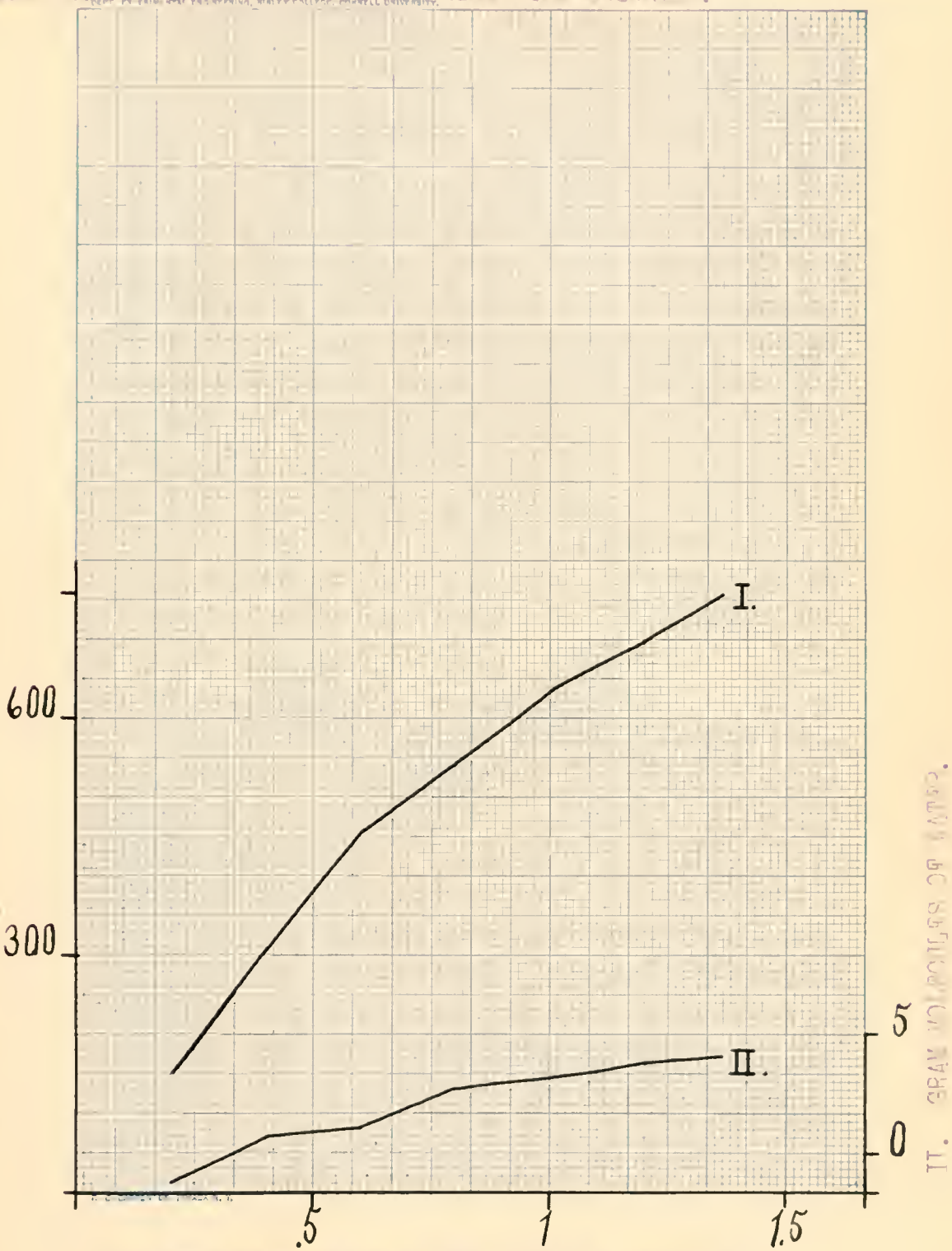

FIGURE XVIII.

The effect of decrease in the amount of water present as solvent is plainly shown in the diminishing values of M as the amount of solvent is lessened. The slight irregularities are probably due to unavoidable experimental error, and inaccuracy of the conductivity method as a measurs of its sociation.

Thus far all of the Salts Studied have a Common Anion. In order to Extend the Investigation to a Pair of Salts having a Common Cation, a Mixture of Calcium Nitrate and Calcium chloride was employed.

The data for the separate solutions of these two salts has already been given. The results obtained with the mixture follow.

Table CII. FREEZING-POINT MEASUREMENTS.

m.	P.	Δ.
0.5 Ca_2NO_3 0.5 $CaCl_2$	1 "	2°50
0.9 Ca_2NO_3 0.9 $CaCl_2$	1 "	4.88
1.3 Ca_2NO_3 1.3 $CaCl_2$	1 "	7.67
1.7 Ca_2NO_3 1.7 $CaCl_2$	1 "	11.00
2.1 Ca_2NO_3 2.1 $CaCl_2$	1 "	14.78
2.5 Ca_2NO_3 2.5 $CaCl_2$	1 "	19.2
2.9 Ca_2NO_3 2.9 $CaCl_2$	1 "	24.2
3.31102 Ca_2NO_3 3.31102 $CaCl_2$	1 "	30.7

[illegible]

The effect of increase in the number of [illegible] [illegible] is [illegible] shown in the accompanying [illegible] [illegible] of [illegible] is indicated. The [illegible] [illegible] [illegible] may possibly due to [illegible] [illegible] [illegible] [illegible] of the sensitivity method in a measure of [illegible] [illegible].

These are all of the data [illegible] [illegible] [illegible] [illegible]

Table CIII. CONDUCTIVITY MEASUREMENTS.

m.	P.	m_c.	v_c.	k_w	k.	D.	k_c.	Λ_v.	α.
0.5 $Ca(NO_3)_2$	1	0.25	4.0000	.039475	.020975	.05573	.018254	73.0	0.547
0.5 $CaCl_2$	"	"	"		.024073		.021281	84.9	.575
0.9 $Ca(NO_3)_2$	1	0.45	2.2222	.059937	.03259	.013010	.026780	59.5	.442
0.9 $CaCl_2$	"	"	"		.039688		.033157	73.7	.499
1.3 $Ca(NO_3)_2$	1	0.65	1.538	.073550	.042932	.023618	.030833	47.4	.353
1.3 $CaCl_2$	"	"	"		.054236		.042716	65.7	.445
1.7 $Ca(NO_3)_2$	1	0.85	1.1765	.081797	.050272	.035378	.031691	37.3	.277
1.7 $CaCl_2$	"	"	"		.066903		.050106	59.0	.400
2.1 $Ca(NO_3)_2$	1	1.05	0.9523	.08410	.056501	.050445	.029266	27.9	.207
2.1 $CaCl_2$	"	"	"		.078344		.054834	52.2	.354
2.5 $Ca(NO_3)_2$	1	1.25	0.8000	.083681	.060363	.066535	.023751	19.0	.141
2.5 $CaCl_2$	"	"	"		.088853		.058930	47.1	.320
2.9 $Ca(NO_3)_2$	1	1.45	.68966	.077154	.063236		.016375	11.[illegible]	.084
2.9 $CaCl_2$	"	"	"		.097385	.083467	.060780	41.[illegible]	.284
3.311 $Ca(NO_3)_2$	1	1.6555	.60405	.069855	.064674	.098121	.008650	[illegible].2	.039
" $CaCl_2$	"	"	"		.00330		.061203	37.0	.251

Table CIV. WEIGHT-NORMAL CORRECTIONS.

m.	P.	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction Per Cent.
0.5 Ca_2NO_3 0.5 $CaCl_2$	1 atm.	26.3336	1.7197	24.6139	1.5
0.9 Ca_2NO_3 0.9 $CaCl_2$	1 atm.	27.3415	3.0954	24.2461	3.0
1.3 Ca_2NO_3 1.3 $CaCl_2$	1 atm.	28.3615	4.4711	23.8904	4.4
1.7 Ca_2NO_3 1.7 $CaCl_2$	1 atm.	29.3082	5.8469	23.4613	6.2
2.1 Ca_2NO_3 2.1 $CaCl_2$	1 atm.	30.2933	7.326	23.0707	7.7
2.5 Ca_2NO_3 2.5 $CaCl_2$	1 atm.	31.2197	8.5984	22.6213	9.5
2.9 Ca_2NO_3 2.9 $CaCl_2$	1 atm.	32.1762	9.9741	22.2021	11.2
3.3111 Ca_2NO_3 3.311 $CaCl_2$	1 atm.	33.0792	11.3878	21.6914	13.2

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[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
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[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
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[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

Table CV. HYDRATES.

m.	P.	m_c.	α.	L_c.	M.	Δ.	WT. Normal Cor.	M_c.	H_c.
0.5 $Ca2NO_3$	1	0.25	0.543	3.88	6.3	2°50	1.5	4.6	18.4
0.5 $CaCl_2$	"	"	.575	4.00	8.2			7.0	28.0
0.9 $Ca2NO_3$	1	0.45	.442	3.51	8.0	4.88	3.0	7.4	16.4
0.9 $CaCl_2$	"	"	.499	3.72	11.7			11.2	24.9
1.3 $Ca2NO_3$	1	0.65	.353	3.17	10.5	7.67	4.4	9.5	14.8
1.3 $CaCl_2$	"	"	.445	3.52	15.7			15.1	23.2
1.7 $Ca2NO_3$	1	0.85	.277	2.89	13.1	11.00	6.2	13.1	14.2
1.7 $CaCl_2$	"	"	.400	3.35	18.9			18.2	21.4
2.1 $Ca2NO_3$	1	1.05	.207	2.63	15.7	14.78	7.7	14.1	13.4
2.1 $CaCl_2$	"	"	.354	3.18	21.9			20.6	19.8
2.5 $Ca2NO_3$	1	1.25	.141	2.39	18.4	19.20	9.5	16.4	13.1
2.5 $CaCl_2$	"	"	.320	3.05	24.3			22.8	18.2
2.9 $Ca2NO_3$	1	1.45	.084	2.17	20.4	24.2	11.2	17.6	12.1
2.9 $CaCl_2$	"	"	.284	2.92	27.3			25.2	17.4
					22.4				
3.311 $Ca2NO_3$	1	1.6555	.039	2.01	22.4	30.7	13.2	16.4	9.9
3.311 $CaCl_2$	"	"	.251	2.79	30.1			25.6	15.5

CALCIUM CHLORIDE ALONE.
" " MIXED WITH CALCIUM NITRATE.
" NITRATE ALONE.
" " MIXED WITH CALCIUM CHLORIDE.

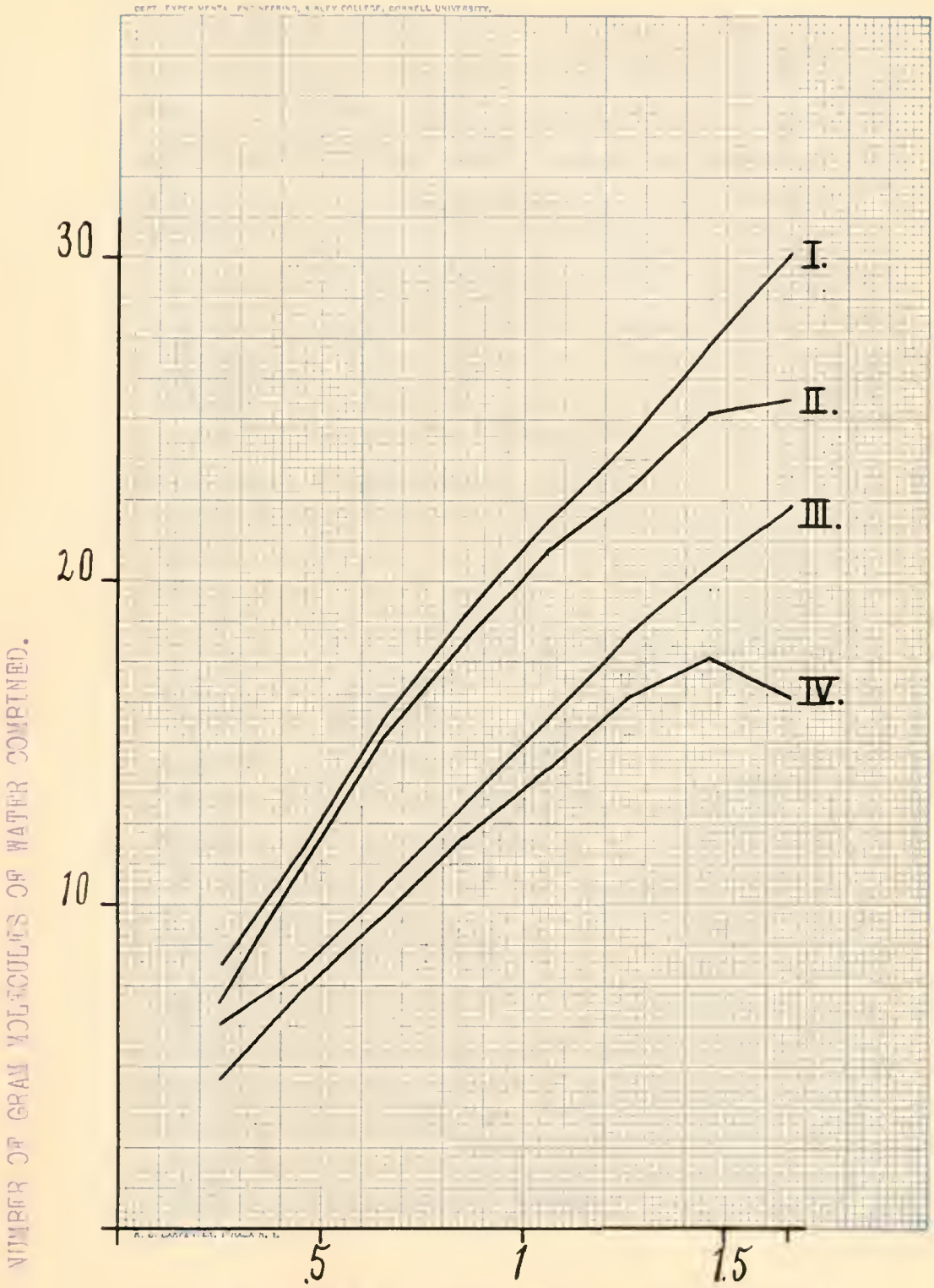

FIGURE XIX.

The above values of M are plotted in curves in Figure XIX. The results are of the same character as those shown by the preceding mixtures. The most concentrated solution measured shows a somewhat lower value for M in the mixture than we should expect, but it must be borne in mind that at this great concentration the experimental errors involved are necessarily very large.

Tables CVI and CVII contain the data necessary to compare the change in the amount of solvent present with the change in the values of M in separate solution and in the mixture.

Table CVI. CALCIUM CHLORIDE IN MIXTURE OF CALCIUM NITRATE AND CALCIUM CHLORIDE.

m.	D_{H_2O}.	D_M.
0.25	92	1.2
0.45	153	0.5
0.65	202	0.6
0.85	260	0.7
1.05	306	1.1
1.25	358	1.5
1.45	392	2.1
1.6555	386	4.5

[illegible] values of [illegible] studied in moving [illegible] [illegible]. The results are of the same nature - [illegible] [illegible] [illegible] [illegible]. The best [illegible] [illegible] [illegible]

Table CVII. CALCIUM NITRATE IN MIXTURE OF CALCIUM NITRATE AND CALCIUM CHLORIDE.

m.	D_{H_2O}.	D_M.
0.25	131	1.7
0.45	213	0.6
0.65	288	0.9
0.85	350	1.0
1.05	404	1.6
1.25	447	2.0
1.45	496	2.8
1.6555	575	6.0

These values are plotted in curves in Figures XX and XXI. A diminution in the amount of water present as solvent causes a diminution in the value of M. This effect appears to be greater with increasing concentration. It is probable that in the most dilute solutions the difference in the hydrating power of theions and molecules affects the curve. changing its direction.

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[illegible]	[illegible]	[illegible]
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[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
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[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]

These values are plotted in series in Figures [illegible] and [illegible]. A comparison of the [illegible] of [illegible] shows a [illegible] increase in [illegible] with the value of [illegible]. This effect results in an [illegible] with increasing [illegible]. It is apparent that in the [illegible] model [illegible] the difference in the [illegible] under [illegible] of [illegible] and [illegible] affecting the [illegible] [illegible] the difference.

DIFFERENCE BETWEEN THE ABILITY OF WATER ACTING AS SOLVENT TOWARD THE CALCIUM NITRATE IN THE MIXTURE OF CALCIUM NITRATE AND CALCIUM CHLORIDE AND BY THE SEPARATE SOLUTION OF CALCIUM NITRATE.

DIFFERENCE BETWEEN THE VALUES OF i FOR CALCIUM NITRATE IN SEPARATE SOLUTION AND IN THE MIXTURE OF CALCIUM NITRATE AND CALCIUM CHLORIDE.

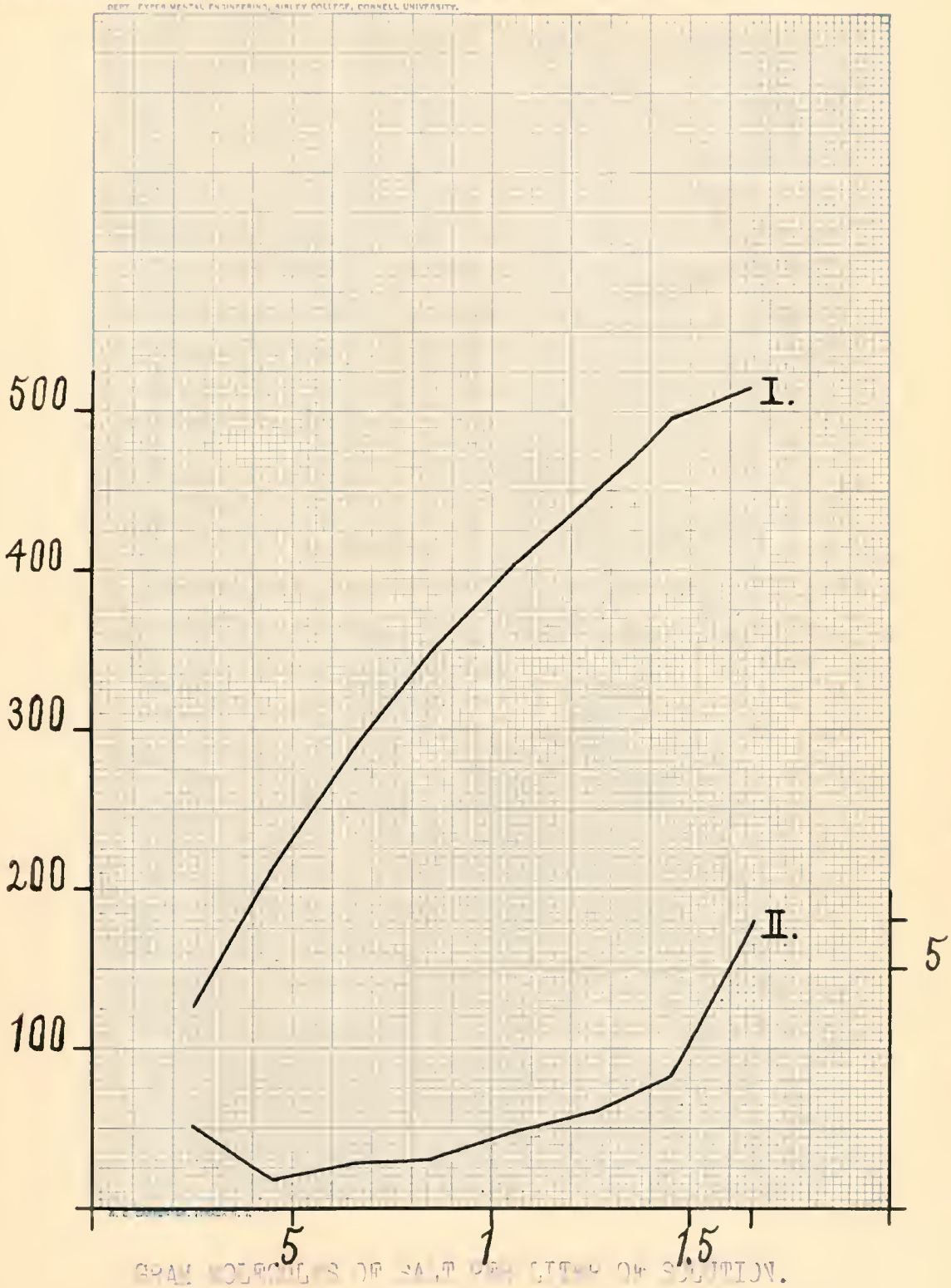

FIGURE XX.

DIFFERENCE BETWEEN THE AMOUNT OF WATER ACTING AS SOLVENT TOWARD THE CALCIUM CHLORIDE IN THE MIXTURE OF CALCIUM NITRATE AND CALCIUM CHLORIDE AND IN THE SEPARATE SOLUTION OF CALCIUM CHLORIDE.

DIFFERENCE BETWEEN THE VALUES OF W FOR CALCIUM CHLORIDE IN SEPARATE SOLUTION AND IN THE MIXTURE OF CALCIUM NITRATE AND CALCIUM CHLORIDE.

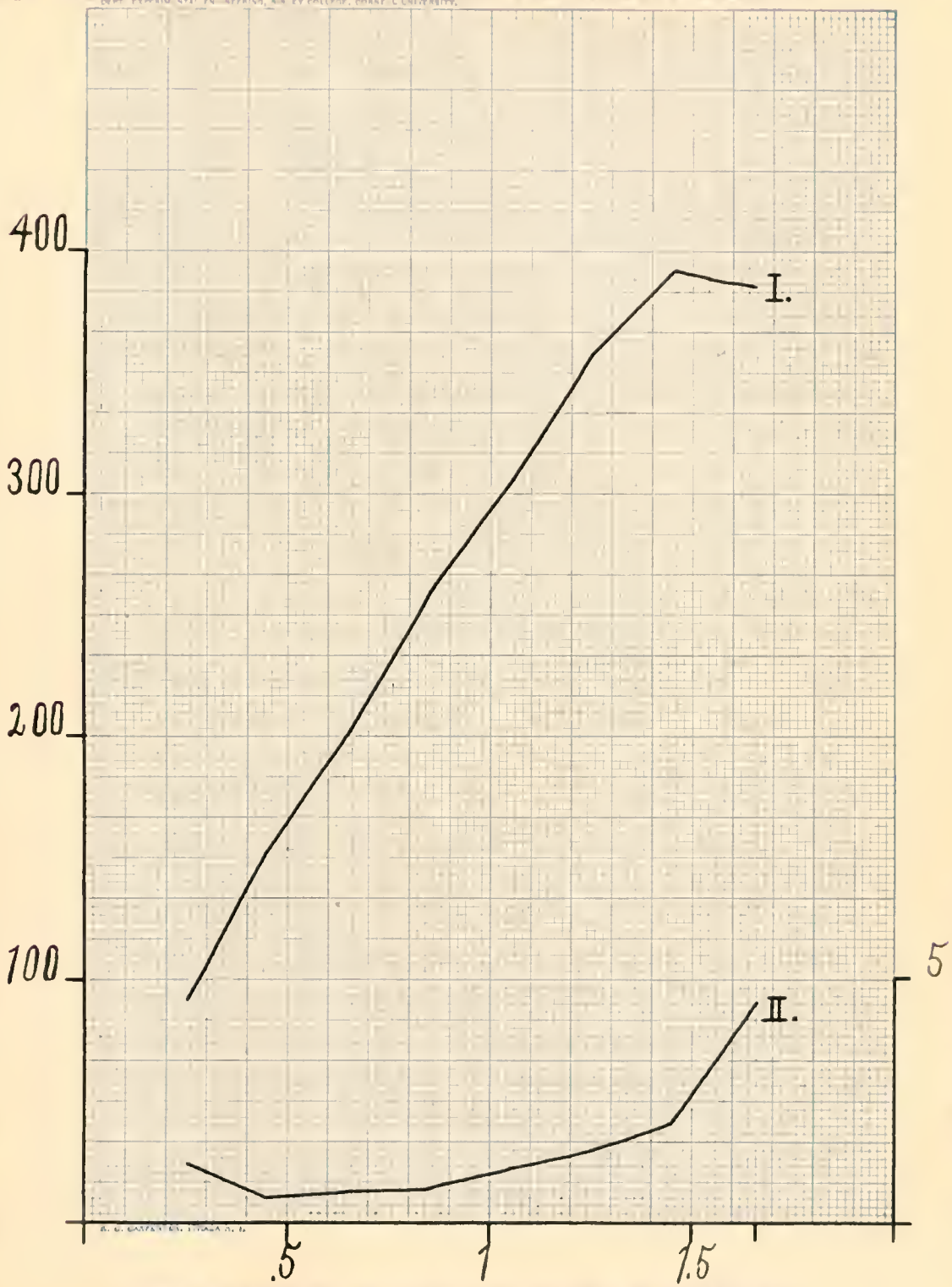

FIGURE XVI.

THE EFFECT OF CHANGE IN TEMPERATURE UPON THE CONDUCTIVITIES OF SEPARATE SOLUTIONS OF ELECTROLYTES AND UPON MIXTURES OF THESE ELECTROLYTES.

In this paper we have repeatedly called attention to the fact that the conductivity method furnishes us with only an approximate value of the dissociation of a salt. The conductivity method of measuring dissociation is, however, the mose general one available. In order to study the effect of change of temperature upon the conductivities of separate solutions of electrolytes, and upon mixtures of these electrolytes it was necessary to select a pair of salts which do not form double salts in solution, and which have little or no hydrating power. Potassium chloride and ammonium chloride were employed.

The conductivities of single solutions of these salts and of their mixtures were studied at 0° and 12°. Comparison having shown that our values agree very closely with those obtained by Jones and West[1] and Jones and Knight[2], Jones and Knight's values at 25° were used. The values of Jones and West, at 18°, show a very close agreement with those obtained experimentally by Kohlrausch at the same temperature. The

1. Amer. Chem. Journ. 34, 481 (1905)
2. " " " 22, 125 (1899).

values for potassium chloride at 25° are taken from the results of Kohlrausch.

POTASSIUM CHLORIDE.

Table CVIII. MOLECULAR CONDUCTIVITIES.

v.	μ_v 0°.	μ_v 12°.	v.	μ_v 25°.
1	61.58	82.05	1	104.1
2	63.02	84.43	2	108.6
5	65.85	87.84	4	111.2
20	68.59	93.88	16	121.5
100	72.13	98.69	80	128.5
200	73.73	101.3	160	131.1
1000	74.31	103.3	640	137.9

AMMONIUM CHLORIDE.

Table CIX. MOLECULAR CONDUCTIVITIES.

v.	μ_v 0°.	μ_v 12°.	v.	μ_v 25°.
1	61.08	81.15	1	99.3
2	62.53	83.57	2	104.9
5	65.98	87.66	4	110.4
20	68.13	95.19	16	120.9
100	71.64	99.94	80	131.8
200	72.89	101.3	160	134.2
1000	74.10	103.7	640	138.1

Since we are employing some of the values of Jones and West, Jones and Knight and Kohlrausch, at 25°, we have tabulated a few values taken from these sources side by side with our own.

POTASSIUM CHLORIDE.

Table CX. COMPARISON OF CONDUCTIVITIES.

v.	Ours.	Jones and West.	(Jones and West.)	Kohlrausch.
	μ_v 0°.	μ_v 0°.	μ_v 18°.	μ_v 18°.
1	61.58	----	---	---
2	63.02	62.96	95.9	95.8
5	65.85	----	---	---

[illegible] the [illegible] [illegible] [illegible]

Table CX. COMPARISON OF CONDUCTIVITIES. (Cont.)

v.	μ_v 0°.	μ_v 0°.	μ_v 18°.	μ_v 18°.
8	---	66.47	103.6	----
16	---	68.4	107.0	----
20	68.59	---	----	108.3
32	---	70.27	110.7	----
120	72.13	---	----	114.7
128	---	73.0	115.5	----
200	73.73	---	----	----
1000	74.31	---	----	119.3
1024	---	75.14	119.3	----

AMMONIUM CHLORIDE.

Table CXI. COMPARISON OF CONDUCTIVITIES.

v.	Ours. μ_v 0°.	Jones West. μ_v 0°.	Jones West. μ_v 18°.	Kohlrausch. μ_v 18°.
1	61.06	----	----	----
2	62.53	62.76	96.3	94.8
5	63.98	----	----	----
8	----	66.17	103.6	----
16	----	68.02	107.2	----
20	68.13	----	----	107.8
32	----	70.2	110.8	----
100	71.64	----	----	114.2
128	----	73.08	116.2	----
200	72.89	----	----	----
1000	74.10	----	----	119.0
1024	----	74.84	119.6	----

Table CXII. COMPARISON OF CONDUCTIVITIES.

v.	Jones and West. μ_v 25°.	Jones and Knight. μ_v 25°.
1	----	99.3
2	109.2	104.9
8	118.6	115.8
16	123.2	120.9
32	127.6	125.5
128	133.4	----
160	----	134.2
512	136.8	----
640	----	138.1
1024	137.8	----
1600	----	138.9

In connection with the conductivity of ammonium chloride, Jones and Knight say[1]; "The values which we found for the conductivity of ammonium chloride differed slightly from those obtained by Kohlrausch[2], our values being somewhat lower in the more concentrated solutions, and a little higher in the more dilute. This difference is probably due to the temperature coefficient which must be added to Kohlrausch's values, to transform them from 18° to 25°." This coefficient was uncertain over any considerable range of temperature.

POTASSIUM CHLORIDE.

Table CXIII. COMPARISON OF CONDUCTIVITIES.

v.	Jones and West. μ_v 25°.	Jones and Knight. (Kohlrausch). μ_v 25°.
1	----	104.5
2	109.5	108.6
8	118.6	116.5
16	122.9	121.5
32	126.8	125.4
128	132.4	----
160	----	131.1
512	135.5	----
640	----	133.9
1024	137.0	----
1600	----	135.4

From these tables it is evident that our values agree very well with those of Kohlrausch, Jones and West, and Jones and Knight.

1. Amer. Chem. Journ, 22, 117 (1899).
2. Ann. Phys. (Wied.), 26, 161.

Let us turn, now, to the conductivities of the mixtures of potassium chloride and ammonium chloride. These solutions were mixed in equal volumes. When, for example, a 2.0 N solution of potassium chloride is added to an equal volume of 2.0 N ammonium chloride, the assumption that the resulting solution consists of 1.0 N potassium chloride and 1.0 N ammonium chloride is evidently not quite correct, because of the volume occupied by the salt in the added solution. In order to make the necessary correction for this factor, pycnometer measurements were made in the more concentrated solutions. In the more dilute solutions this factor is so small that it is entirely negligible.

In the following table, m is the normality; C is the capacity of the pycnometer in cubic centimeters; W_{Salt} is the weight of salt present in the solution; W_{H_2O} is the weight of water present in the volume of solution contained in the pycnometer, and V is the volume of water in a thousand cubic centimeters of the solution.

Table CXIV. POTASSIUM CHLORIDE. AT 12°.

m.	C.	W_{Salt}.	W_{H_2O}.	V.
0.05	24.4259	0.0911	24.3821	998.66
0.20	23.9474	0.35373	23.8077	994.62
0.50	11.6945	0.4362	11.5294	986.35
1.00	12.6976	0.9473	12.3370	972.16

[illegible]

[illegible]

[illegible]

Table CXV. AMMONIUM CHLORIDE. AT 12°.

m.	C.	$W_{Salt.}$	W_{H_2O}.	V.
0.2	24.3605	0.2608	24.0679	992.54
0.4	24.4259	0.5229	24.0573	985.37
0.6	23.9474	0.7690	23.4098	978.00
0.8	12.6976	0.5137	12.3176	970.52
1.0	11.6915	0.6259	11.2574	963.07

Based upon these measurements, the conductivity of the potassium chloride and ammonium chloride in the various mixtures was calculated, on the assumption that no change in the dissociation of these salts takes place when their solutions are mixed. The results are given, along with the conductivities obtained experimentally, in the following tables.

Table CXVI. COMPARISON FOR POTASSIUM CHLORIDE, AMMONIUM CHLORIDE.

v.	KCl μ_v 25°.	v.	NH_4Cl μ_v 25°.	Sum.	v.	KCl.NH_4Cl μ_v 25°.	Difference.
1	104.1	1	99.3	203.4	1	179.3	24.1
2	108.6	2	104.9	213.5	2	195.0	18.5
4	111.2	4	110.4	221.6	4	208.3	13.3
8	116.5	8	115.8	232.3	8	220.9	11.4
16	121.5	16	120.9	242.4	16	231.7	10.7
32	125.4	32	125.3	250.7	32	241.2	9.5
40	125.7	40	127.6	253.3	40	245.9	7.4
80	128.5	80	131.8	260.3	80	254.3	6.0
160	131.1	160	134.2	265.3	160	263.3	3.0
320	132.1	320	136.8	268.9	320	267.0	1.9
640	133.9	640	138.1	272.0	640	273.1	-1.1
1600	135.4	1600	138.9	274.3	1600	279.1	-4.8

[illegible]

Table CXVII. COMPARISON FOR POTASSIUM CHLORIDE, AMMONIUM CHLORIDE. (Jones and Knight).

KCl		NH_4Cl			KCl.NH_4Cl		Difference.
v.	μ_v 25°.	v.	μ_v 25°.	Sum.	v.	μ_v 25°.	
1	81.95	1	81.10	163.1	1	154.9	8.2
2	84.38	2	83.55	167.9	2	161.1	6.8
5	87.82	5	87.66	175.5	5	170.5	5.0
20	92.88	20	93.19	186.1	20	181.3	4.8
100	98.69	100	99.94	198.6	100	194.7	3.9
200	101.3	200	101.3	202.6	200	199.7	2.9
1000	103.3	1000	103.7	207.	1000	208.7	-1.7

Table CXVIII. COMPARISON FOR POTASSIUM CHLORIDE, AMMONIUM CHLORIDE.

KCl		NH_4Cl	Sum.		KCl.NH_4Cl	
v.	μ_v 0°.	v.	μ_v 0°.	v.	μ_v 0°.	Difference.
1	61.48	1	61.03	122.5	121.2	1.3
2	62.97	2	62.51	125.5	122.8	2.7
5	65.83	5	63.97	129.8	126.9	2.9
20	68.59	20	68.13	136.7	133.4	3.3
100	72.13	100	71.64	143.8	141.2	2.6
200	73.73	200	72.89	146.6	144.9	1.7
1000	74.81	1000	74.10	148.4	147.5	0.9

Table CXIX. COMPARISON OF DIFFERENCES.

v.	Diff. 0°.	Diff. 12°.	Diff. 25°.
1	1.3	8.2	24.1
2	2.7	6.8	18.5
5	2.9	5.0	12.8
20	3.3	4.8	10.1
100	2.6	3.9	5.2
200	1.7	2.9	2.7
1000	0.9	-1.7	-2.5

If this change in the conductivity when the solutions are mixed is due only to a suppression of ionization, then we should expect the suppression to be nearly the same at the various temperatures, since the dissociation is very nearly the same at these various temperatures. (vid. Tables CXX, CXXI).

Table CXX. DISSOCIATION OF POTASSIUM CHLORIDE.

v.	α 0°	α 12°	α 25°
1	0.827	0.798	0.768
2	.847	.817	.802
5	.886	.850	.831
20	.923	.899	.905
100	.971	.955	.954
200	.992	.981	.970
1000	1.00	1.00	.993

Table CXXI. DISSOCIATION OF AMMONIUM CHLORIDE.

v.	α 0°	α 12°	α 25°
1	0.824	0.782	0.715
2	.844	.806	.755
5	.863	.845	.805
20	.919	.899	.878
100	.967	.964	.953
200	.984	.977	.970
1000	1.00	1.00	.997

If the suppression of the ionization is the cause of the diminution in the conductivity when the solutions are mixed, then the greatest diminution should take place where the more highly dissociated salts are mixed; that is, the diminution in conductivity should be slightly greater at 0° than at 12°, and slightly greater at 12° than at 25°. Just the opposite is shown by Table CXIX to be true. Again, if this lessening of conductivity is dependent upon the amount of dissociation alone, then since the difference between the dissociation at 0° and 12° is the same or a little greater than the difference between the dissociation at 12° and 25°, (save in some cases in the ammonium chloride) we should expect to find the difference between the col-

[illegible]

[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]

[illegible]

[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]

[illegible]

umns headed Diff.12° and Diff.0°, in Table CXIX, the same or slightly greater than the difference between the columns headed Diff. 12° and Diff. 25°. The opposite is true—the difference between columns #2 and #3 being from two to four times as great as that between #1 and #2, up to v = 100. At v = 100 the differences are the same, and at v = 200 and v = 1000 the column headed Diff.25° becomes smaller than the other two.

We must, then, look elsewhere for the cause of the change in the conductivities, since it is evidently not due solely to change in dissociation. There are three other factors which might come into play:—Change in hydration, giving rise to a change in the dimensions of the ionic sphere; change in the viscosity of the solution with change in temperature; change in the number of the dissolved particles (ions and molecules). Of these three possibilities, the first probably does not affect the conductivity appreciably, there being little hydration. The second is probably the principal factor in causing changes in the conductivity with changes in the temperature. The third—change in the number of the dissolved particles—may also play some part, since the value of α becomes smaller with risein temperature, and, other things

being equal, the fewer the number of ions and molecules with which a moving ion must collide, the less the friction it will encounter. The differences in the values of columns #1, #2 and #3 are greatest for the most concentrated solutions, and it is in these solutions that the greatest change in the value α is noted, with rise in temperature.

Clearly, values for α which are based upon the conductivity of the completely dissociated molecule at high dilution, cannot be correct, since the conductivity of this completely dissociated molecule must be considerably altered by change in viscosity, and by change in number of dissolved ions or molecules, both of which factors enter, on increase in the concentration; the number of ions and molecules present undergoing especially great alteration.

SUMMARY.

It has been shown:

1. That the complexity of the hydrates formed by a salt is directly proportional to the amount of water present as solvent.

2. That when two salts are present in the same solution the complexity of the hydrates is somewhat less than in separate solutions of these salts, each salt tending to dehydrate the other.

3. That the ions and the molecules of salts probably have dif-

ferent hydrating power.

4. That the hydrating power of the molecules is probably greater than that of the ions into which these molecules dissociate in solution.

5. Additional proof is furnished for the hypothesis that the conductivity method is by no means an accurate measure of dissociation.

6. It has been pointed out that the diminution in conductivity, which takes place when two electrolytes of the above type are mixed, is probably not due entirely, or even principally, to suppression of the ionization, but to,

A. Changes in the viscosity of the solvent;

B. To changes in the number of dissolved ions and molecules;

C. To change in the size of the ionic sphere due to alteration in the amount of water ~~with~~ which the ion must drag with it through the solution.

[illegible] Questions [illegible]:

a. What is [illegible] where of the [illegible] is [illegible] [illegible] [illegible] of the [illegible] [illegible] [illegible]

BIOGRAPHY.

Charles M. A. Stine was born in Norwich, Connecticut, on October 18, 1882. His preparatory training was received in public schools and academies, in various states. He entered Pennsylvania College in 1897, where he received the degree of A.B. in 1901. In 1902 he returned to Pennsylvania College for special work in Chemistry, receiving the degree of B.S. in 1903, that of A.M. in 1904 and that of M.S. in 1906. During the two years preceding his enrollment in the Johns Hopkins University he taught Chemistry and Mathematics in Maryland College.

In October, 1905, he entered the Johns Hopkins University as a graduate student in Chemistry, with Physical Chemistry and Mineralogy as subordinate subjects. The most of his time was devoted to Physical Chemistry, and his dissertation was prepared in this field. In 1906-1907 he held a Fellowship in Chemistry at the University.